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AN INTRODUCTION TO THE STUDY

OF THE

COMPOUNDS OF CARBON

OR

ORGANIC CHEMISTRY

BY

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FOURTH REVISION

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PREFACE TO FIRST EDITION.

This book is intended for those who are beginning the subject. For this reason, special care has been taken to select for treatment such compounds as best serve to make clear the fundamental principles. General relations as illustrated by special cases are discussed rather more fully than is customary in books of the same size; and, on the other hand, the number of compounds taken up is smaller than usual. The author has endeavored to avoid dogmatism, and to lead the student, through a careful study of the facts, to see for himself the reasons for adopting the prevalent views in regard to the structure of the compounds of carbon. Whenever a new formula is presented, the reasons for using it are given so that it may afterward be used intelligently. It is believed that the book is adapted to the needs of all students of chemistry, whether they intend to follow the pure science, or to deal with it in its applications to the arts, medicine, etc. It is difficult to see how, without some such general introductory study, the technical chemist and the student of medicine can comprehend what is usually put before them under the heads of "Applied Organic Chemistry" and "Medical Chemistry."

Without some direct contact with the compounds considered, it is impossible to get a clear idea regarding them and their changes. A course of properly selected experiments, illustrating the methods used in preparing the principal classes of compounds, and the fundamental reactions involved in their transformations, wonderfully facilitates the study. The attempt has been made to give directions for such a course. More than eighty experiments which could be performed in any chemical laboratory are described; and it is hoped that the plan may meet with approval. The time required to perform a fair proportion of these experiments is not great; and the results in the direction of enlarging the student's knowledge of chemical phenomena, will, it is firmly believed, furnish a full compensation for the time spent.

The order in which the topics are taken up will be found to differ somewhat from that commonly adopted. The object in view was, however, not to find a new method, but to find one which would bring out as clearly as possible the beauty and simplicity of the relations which exist between the different classes of carbon compounds. The reasons for the method used are given in the body of the book.

PREFACE TO FOURTH REVISION.

THE important advances that have been made in the field of organic chemistry during the past few years have made a thorough revision of this book necessary. The present edition gives the results of the revision. The principal changes and additions will be found in the chapters dealing with the Sugars, Stereoisomerism, the Diazo Compounds, and the Terpenes. The treatment of the Aromatic Compounds is, in general, fuller than in the older editions. Although considerable has been added, the size of the volume has not been markedly increased, the difference between the last edition and the present being only about fifty pages. In addition to the changes indicated above, minor changes have been made throughout, and the author believes that the book is now fully in harmony with the present state of organic chemistry.

JANUARY, 1903.

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CHEMISTRY

OF THE

COMPOUNDS OF CARBON.

CHAPTER I.

INTRODUCTION.

In studying the compounds of carbon, one cannot fail to be struck by their large number, and by the ease with which they undergo change when subjected to various influences. Mainly on account of the large number, though partly on account of peculiarities in their chemical conduct, it is customary to treat of these compounds by themselves. At first, *General Chemistry* was divided into *Inorganic* and *Organic Chemistry*, as it was believed that there were fundamental differences between the compounds included under the two heads. Those compounds which form the mineral portion of the earth were treated under the first head, while those which were found ready formed in the organs of plants or animals were the subject of organic chemistry. It was believed that, as the organic compounds are elaborated under the influence of the life process, there must be something about them which distinguishes them from the inorganic compounds in whose formation the life process has no part. Gradually, however, this idea has been abandoned; for, one by one, many of the compounds which are found in plants and animals have been made in the chemical laboratory, and without the aid of the life process. The first instance of the preparation of an organic compound by an artificial method was that of urea. This substance was obtained by Wöhler in 1828 from ammonium cyanate. When a water solution of the latter is allowed to evaporate, urea

is deposited. Up to the time of Wöhler's discovery, the formation of urea, like that of other organic compounds, was thought to be intimately and necessarily connected with life; but it was thus shown that it could be formed without the intervention of life. Afterward, it was shown that potassium cyanide can be made by passing nitrogen over a heated mixture of carbon and potassium carbonate; and, as potassium cyanate can be made from the cyanide by oxidation, it follows that urea can be made from the elements. Finally, in 1856, Berthelot succeeded in making potassium formate by passing carbon monoxide over heated potassium hydroxide; and in making acetylene, a compound, the composition of which is represented by the formula C_2H_2, by passing electric sparks between electrodes of carbon in an atmosphere of hydrogen. Since that time, every year has witnessed the artificial preparation, by purely chemical means, of compounds of carbon which are found in the organs of plants and animals.

It hence appears that the formation of the compounds of carbon is not dependent upon the life process; that they are simply chemical compounds governed by the same laws that govern other chemical compounds; and the name, *Organic Chemistry*, signifying, as it does, that the compounds included under it are necessarily related to organisms, is misleading. Organic chemistry is nothing but the *Chemistry of the Compounds of Carbon*. It is not a science independent of inorganic chemistry, but is just as much a part of chemistry as the chemistry of the compounds of sodium, or of the compounds of silicon, etc.

The name *Chemistry of the Compounds of Carbon* has been objected to as being too broad. Strictly speaking, this title includes the carbonates, and it is customary to treat of these widely distributed substances under the head of Inorganic Chemistry. Most books on Inorganic Chemistry also deal with some of the simpler compounds of carbon, such as the oxides, cyanogen, marsh gas, etc.

This objection is of weight only as far as the carbonates are concerned, and it does not appear strong enough to make the introduction of a new name necessary. It should be mentioned, however, that the name *Chemistry of the Hydrocarbons and their Derivatives* has been suggested. The exact significance of this name will appear when the compounds with which we shall have to deal come up for consideration.

Sources of compounds. — The compounds of carbon are, for the most part, made in the laboratory; but in preparing them we usually start with a few fundamental compounds that are formed by natural processes. A large number, such as the sugars, starch, cellulose, and the alkaloids, of which morphine, quinine, and nicotine are examples, occur ready formed in plants, but always mixed with other substances. Others, such as urea, uric acid, albumin, etc., occur in animal organisms. *Petroleum*, which has been formed in nature by processes, the exact nature of which has not yet been satisfactorily explained, contains a large number of compounds consisting of only carbon and hydrogen; and these compounds serve as the starting-points in the preparation of a large number of derivatives. When coal is heated for the purpose of manufacturing illuminating gas, a very complex mixture of liquid and solid products is obtained as a by-product, known as *coal tar*. This substance yields some of the most valued compounds of carbon. A larger number of the compounds of carbon are obtained from this than from any other one source. When bones are heated in the manufacture of bone-black, an oil known as *bone oil* is obtained. This also has proved to be the source of a large number of interesting compounds. In the preparation of charcoal by heating wood, the liquid products are sometimes condensed, and they form the source of several important compounds, among which may be mentioned *wood spirits* or *methyl alcohol*, *acetone*, and *pyroligneous* or *acetic acid*.

Finally, we are dependent upon the process known as *fermentation* for a number of the most important compounds of carbon. Fermentation, as will be shown, is a general term, signifying any process in which a change in the composition of a body is effected by means of minute animal or vegetable organisms. The best known example of fermentation is that of sugar, which gives rise to the formation of ordinary *alcohol*. Alcohol in turn serves as the starting-point for the preparation of a large number of compounds.

Purification of the compounds. — Before the natural compounds of carbon can be studied chemically, they must, of course, be freed from foreign substances; and before the constituents of the complex mixtures, petroleum, coal tar, and bone oil can be studied, they must be separated and purified. The processes of separation and purification are, in many cases, extremely difficult. If the substance is a solid, different methods may be used according to the nature of the substance. *Crystallization* is more frequently made use of than any other process. This is well illustrated, on the large scale, in the refining of sugar, which consists, essentially, in dissolving the sugar in water, filtering through bone-black, which absorbs coloring matter, and then evaporating down to crystallization. When two or more substances are found together, they may, in many cases, be separated by what is called *fractional crystallization*. This consists in evaporating the solution until, on cooling, a comparatively small part of the substance is deposited. This deposit is filtered off, and the solution further evaporated; when a second deposit is obtained, and so on to the end. The successive deposits thus obtained are then recrystallized, each separately, until, finally, the deposits are found to be homogeneous.

The chief solvents used are water, alcohol, ether, benzine, and bisulphide of carbon; alcohol being the one most generally applicable.

In the case of liquids, the process of *distillation* is used. The apparatus commonly used is illustrated in Fig. 1.

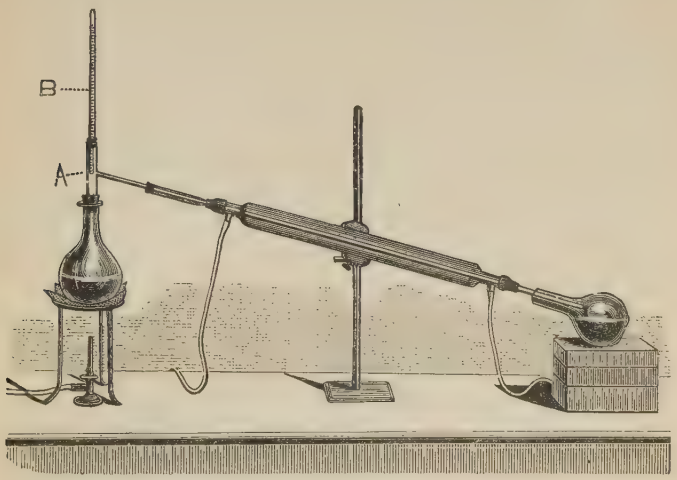


Fig. 1.

The only part of the apparatus that requires explanation is the tube *A*. This is known as the *distilling tube*. It is simply a straight glass tube, about 16^{cm} long and 12 to 14^{mm} in diameter, to which is attached a smaller branch somewhat inclined downward. The object of the tube is to accommodate a thermometer *B*, which is so fixed by means of a cork, that it is in the centre of the larger tube, and its bulb directly opposite the opening of the smaller branch.

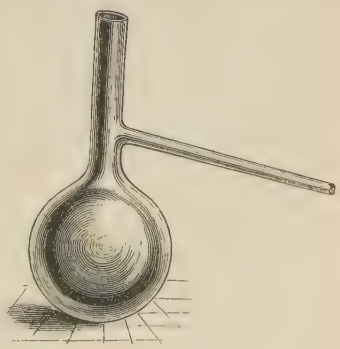


Fig. 2.

For small quantities of liquids, the distilling flask is much used. This is a long-necked, round

flask, with a branch tube fitted directly into the neck, as shown in Fig. 2. In this apparatus, the thermometer is fitted into the neck of the flask in the same relation to the exit tube as in the larger apparatus.

For the separation of liquids of different boiling-points, the process of *fractional* or *partial distillation* is much used. When a mixture of two or more liquids of different boiling-points is boiled, it will be noticed that the boiling-point gradually rises from that of the lowest boiling substance to that of the highest, Thus, ordinary alcohol boils at 78°, and water at 100°. If the two are mixed, and the mixture distilled, it will be found that it begins to boil at 78°, but that very little passes over at this temperature. Gradually, as the distillation proceeds, the temperature indicated by the thermometer becomes higher and higher, until at last 100° is reached, when all distils over. Now the distillates obtained at the different temperatures differ from each other in composition. Those obtained at the lower temperatures are richer in alcohol than those obtained at the higher temperatures, but none of them contains pure alcohol or pure water. In order to separate the two, therefore, we must proceed as follows: A number of clean, dry flasks are prepared for collecting the distillates. The boiling is begun, and the point at which the first drops of the distillate appear in the receiver is noted. That which passes over while the mercury rises through a certain number of degrees (3, 5, or 10, according to the character of the mixture) is collected in the first flask. The receiver is then changed, without interruption of the boiling, and that which passes over while the mercury rises through another interval equal to the first is collected in the second flask. The receiver is again changed, and a third distillate collected; and so on, until the liquid has all been distilled over. It has thus been separated into a number of fractions, each of which has passed over at different temperatures. In the case of alcohol and water, for example, we might have collected distillates from 78° to 83°, from 83° to 88°, from 88° to 93°, from 93° to 98°,

from 98° to 100°. Now a clean distilling flask is taken, and into this the first fraction is poured. This is distilled until the thermometer marks the upper limit of the original first fraction, the new distillate being collected in the flask which contained the first fraction. When this upper limit is reached, the boiling is stopped. It will be found that there is some of the liquid left in the distilling flask. That is to say, assuming that in the first distillation the first fraction was collected between 78° and 83°, on boiling this fraction the second time it will not all come over between these points; when 83° is reached some will be left in the flask. The second fraction is now poured into the distilling flask through a funnel tube, and the boiling is again started. Of the second fraction, a portion will pass over below the point at which it began to boil when first distilled. Collect in the proper flask, and continue the boiling until the thermometer marks the highest point of the fraction last introduced, changing the receiver whenever the indications of the thermometer require it. Now stop the boiling, and pour in fraction No. 3, and so on until all the fractions have been subjected to a second distillation. On examining the new fractions, it will be found that the liquid tends to accumulate in the neighborhood of certain points corresponding to the boiling-points of the constituents of the mixture. The distilling flask is now cleaned, and the whole process repeated. A further separation is thus effected. By continuing the distillation in this way, pure substances can, in most cases, eventually be obtained. That the fractions are pure can be known by the fact that the boiling-points remain constant. In some cases perfect separation cannot be effected by means of fractional distillation; as, for example, in the case of alcohol and water. But still it is valuable, even in such cases, as it enables us to purify the substances, at least partially.

The best examples of distillation carried on on the large scale are those of alcohol and petroleum. Probably the best example of fractional distillation is that of the light oil obtained from coal tar.

Experiment 1. Mix equal parts (about half a litre of each) of alcohol and water. Distil through four or five times, and notice the changes in the quantities obtained in the different fractions.

Determination of the boiling-point. — In dealing with liquids, it often is extremely difficult to tell whether they are pure or not. The first and most important physical property which is utilized for this purpose is the boiling temperature, commonly called the *boiling-point*. This is determined by means of an apparatus, such as is described above as used for distilling. The temperature noted on the thermometer when the liquid is boiling is the boiling-point. When great accuracy is required, the point observed directly must be corrected, in consequence of the expansion of the glass and the cooling of that part of the column of mercury which is not in the vapor. Full directions for making these corrections can be found in larger books. A pure chemical compound always has a constant boiling-point.

Determination of the melting-point. — Just as the boiling-point is a very characteristic property of liquid bodies, so the melting-point is an equally characteristic property of many solid bodies. If a substance begins to melt at a certain temperature, and does not melt completely at that temperature, it is, in all probability, impure. By means of the melting-point minute quantities of impurities, which might readily escape detection by other means, are often found. In dealing with the compounds of carbon, determinations of melting-points are very frequently made. In general, only those compounds which have constant melting-points are to be regarded as pure. The determination is made as follows: Small tubes are prepared by heating a piece of ordinary soft glass tubing of 4^{mm} to 5^{mm} diameter, and drawing it out. If the parts are drawn apart about 12^{cm} to 15^{cm}, two small tubes may be made from the narrowed portion by melting together in the middle, and then filing off each piece where it begins to grow wider near the

large tube. These small tubes must have thin walls, and be of such internal diameter that an ordinary pin can be introduced into them. A small quantity of the substance to be tested is placed in one of the tubes, enough to make a minute column of about 5^{mm} in height. The tube containing the substance is fastened to a thermometer by means of a small rubber band cut from a piece of rubber tubing. The band is placed near the upper part of the tube, and the lower part of the tube, containing the substance, is placed against the bulb of the thermometer. Now a beaker glass of about 100^{cc} capacity is filled with pure paraffin, and the latter melted. When it is in liquid condition, the thermometer, with the tube and substance, is introduced into it, and the heating continued with the aid of a small flame until the substance melts. The instant it melts the temperature indicated by the thermometer is noted. This is the *melting-point* required. It is necessary, however, to correct the observed point in the same way as in the case of the boiling-point. Sometimes, instead of paraffin, concentrated sulphuric acid is used in the bath; and instead of a beaker, a small round-bottomed flask. For substances which melt below 80°, the temperature at which ordinary paraffin is liquid, water or sulphuric acid should be used.

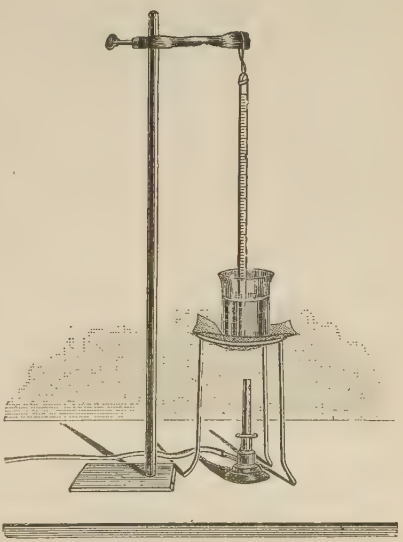


Fig. 3.

Experiment 2. Determine the melting-points of a few substances, such as urea and tartaric acid. If they do not melt at definite points, recrystallize them until they do. Note the melting-points observed,

and see how well they agree with those stated in the book. The arrangement of the apparatus above described is shown in Fig. 3. To secure a uniform temperature of the bath, it should be gently stirred with a glass rod during the experiment. The mercury of the thermometer should rise slowly.

Analysis. — Having purified the compounds, the next step is to determine their composition. A comparatively small number of the compounds ordinarily met with consist of carbon and hydrogen only; the largest number consist of these two elements together with oxygen; many contain carbon, hydrogen, oxygen, and nitrogen. But, in the derivatives of the fundamental compounds, all other elements may occur. Thus the hydrogen may be partly or wholly replaced by chlorine, bromine, or iodine, as in the so-called substitution-products; and any metal may occur in the salts of the acids of carbon. The estimation of carbon and hydrogen is the principal problem in the analysis of the compounds of carbon. This is effected by what is known as the *combustion process*. A known weight of the substance is completely oxidized, the carbon being thus converted into carbon dioxide, and the hydrogen into water. These two products are collected, the carbon dioxide in a solution of potassium hydroxide, the water in calcium chloride, and weighed. From the weights of the products the weights of carbon and hydrogen are calculated. Oxygen, if present, is not estimated directly, but by difference, *i.e.*, the weights of carbon and hydrogen found are added together, and the sum subtracted from the weight of the original substance. The difference represents the weight of the oxygen.

A detailed description of the apparatus and of the method of procedure need not be given here, as it can be found in any book on analytical chemistry. A brief description, however, may not be out of place. The combustion is effected in a hard glass tube which is heated by means of a gas furnace constructed for the purpose. Ordinarily, the substance is placed in a narrow porcelain or platinum vessel, called a *boat*, which is introduced into the tube with granulated copper oxide. The

tube is then connected with (1) a U-tube filled with calcium chloride; (2) a set of bulbs containing a solution of potassium hydroxide, and constructed so as to secure thorough contact of the passing gases with the solution; and (3) a small U-tube filled with solid potassium hydroxide. After the combustion is completed, a current of pure dry oxygen is passed through the tube; and, finally, air is passed until the oxygen is displaced. The method at present used was devised by Liebig. It has contributed very greatly to a thorough understanding of the compounds of carbon.

Two methods are in common use for the estimation of nitrogen in carbon compounds. The first is known as the *absolute method.* This consists in oxidizing the substance by means of copper oxide; then decomposing, by means of highly-heated metallic copper, any oxides of nitrogen which may have been formed, and collecting the nitrogen. The volume of the nitrogen thus obtained is measured, and its weight easily calculated. The chief difficulty in this method consists in removing the nitrogen contained in the apparatus before the combustion is made. The simplest way is to pass pure carbon dioxide through the apparatus until the gas that passes out is completely absorbed by caustic potash. The combustion is then made by heating the tube containing the substance and copper oxide and a layer of copper foil; and, finally, carbon dioxide is again passed through at the end of the operation. The only three gases which can be present, assuming that the substance contained nothing but carbon, hydrogen, oxygen, and nitrogen, are carbon dioxide, water vapor, and free nitrogen. The water vapor is, of course, condensed, and the carbon dioxide is absorbed by passing the gases through a solution of potassium hydroxide, leaving the nitrogen thus alone.

The second method for the estimation of nitrogen consists in heating the substance with a mixture of sodium hydroxide and quicklime, called *soda-lime*, or with sulphuric acid and potassium permanganate. The nitrogen is thus converted into

ammonia, which is collected in a known quantity of dilute hydrochloric or sulphuric acid. After the operation, the amount of acid remaining unneutralized is determined by titration; and from this the amount of ammonia formed can be calculated; and from this, in turn, the amount of nitrogen. This method is not applicable to all compounds, because the nitrogen of some compounds is not converted into ammonia under the circumstances mentioned. The method based upon the use of sulphuric acid and potassium permanganate, known as the Kjeldahl method, is now used almost to the exclusion of other methods.

In regard to the estimation of other constituents of carbon compounds, it need only be said that in most cases it is necessary to get rid of the carbon and hydrogen by some oxidizing process before the estimation can be made. Thus, in estimating sulphur, it is customary to fuse the substance with potassium nitrate and hydroxide, when the carbon and hydrogen are oxidized, and the sulphur is left in the form of potassium sulphate, and can be estimated in the usual way.

Formula. — The deduction of the formula of a compound from the results of the analysis involves two steps. The first is a matter of simple calculation. It is assumed that students who use this book are already familiar with the method of calculating the formula from the analytical results; but an example will, nevertheless, be given. Suppose that the analysis has shown that the substance contains 52.18 per cent carbon, 13.04 per cent hydrogen, and 34.78 per cent oxygen. To get the atomic proportions, divide the figures representing the percentages of the elements by the corresponding atomic weights. We have thus:

	Percentage.		At. Wt.		Relative No. of Atoms.		
C	52.18	÷	12	=	4.35	—	2
H	13.04	÷	1	=	13.04	—	6
O	34.78	÷	16	=	2.17	—	1

That is to say, accepting the atomic weights, 12 for carbon and 16 for oxygen, the simplest figures representing the number of atoms of the three elements in the compound are 2 for carbon,

6 for hydrogen, and 1 for oxygen. According to this, the simplest formula that can be assigned to a substance giving the above results on analysis is C_2H_6O. But the formula $C_4H_{12}O_2$ is equally in accordance with the analytical results, and we can only decide between the two by determining the *molecular weight*. This, as is known, is done by determining the specific gravity of the substance in the form of vapor. This operation is of the greatest importance. It is assumed that the student, who has already studied the elements of inorganic chemistry, is familiar with it, and with the exact connection that exists between it and the molecular weight of the compound. A few statements in regard to the connection will, however, be made here, in order to recall its chief points, and to impress upon the mind of the student its fundamental importance.

Every chemical formula is intended to represent the molecule of a compound and the composition of the molecule. Our conception of the molecule is based almost exclusively on Avogadro's hypothesis, according to which equal volumes of all gases contain the same number of molecules. Hence, by comparing equal volumes of bodies in the form of gas or vapor, we get figures which bear to each other the same relations as the weights of the molecules. The figures called *the specific gravities* express the relations between the weights of equal volumes. In the case of gases, air is taken as the standard, and the weights of other gases are compared with this standard. Thus, if we say that the specific gravity of a gas is 0.918, we mean that if we call the weight of any volume of air 1, that of the same volume of the other gas measured under the same conditions of temperature and pressure is 0.918. If we assign to any compound a certain molecular weight, the molecular weights of other gaseous compounds can be determined without difficulty. We must, therefore, first select some substance, the molecule of which may be used as the standard. Hydrochloric acid is commonly taken, because hydrogen and chlorine unite with each other in only one proportion, and there is good evidence

in favor of the view that it represents the simplest kind of combination, viz., that of one atom of one element with one of another. Hydrogen and chlorine are present in the compound in the proportion of 1 part of hydrogen to 35.4 parts of chlorine; hence the simplest molecular weight that can be assigned to the compound, the atomic weight of hydrogen being 1, is 36.4. The molecular weight of this standard molecule is, therefore, taken to be 36.4, and we have now simply to compare the weights of other gases with that of hydrochloric acid in order to know their molecular weights. Thus, to illustrate by means of the body whose atomic relations we found by analysis to be represented by the formulas C_2H_6O, $C_4H_{12}O_2$, etc., if this body be converted into vapor and its specific gravity determined, it might be found to be 1.6. The relation between the molecular weight of any body and its specific gravity is expressed by the equation

$$M = d \times 28.88,$$

in which M is the molecular weight, and d the specific gravity of the substance in the form of gas or vapor. As d is 1.6 in the case under consideration, we have

$$M\text{(the unknown molecular weight)} = 1.6 \times 28.88 = 46.2.$$

If the formula of the compound is C_2H_6O, the molecular weight, being the sum of the weights of the constituent atoms, is

$$2 \times 12 + 6 \times 1 + 16 = 46,$$

which agrees with the figure deduced from the specific gravity. It therefore follows that the formula C_2H_6O is correct.

There are some other methods which may be used in determining the molecular weight of a compound. Among these may be mentioned the analysis of salts. To illustrate this, take the case of acetic acid. Analysis shows us that it must be represented by one of the formulas CH_2O, $C_2H_4O_2$, $C_3H_6O_2$, etc. If we make the silver salt, we find that its analysis leads us to the formula $C_2H_3O_2Ag$, and not $CHOAg$, and we hence conclude that the molecular formula of acetic acid is $C_2H_4O_2$.

The molecular weight of a substance can also be determined by means of observations on the boiling-points and freezing-points of its solutions. The general facts underlying these determinations are that, in the case of any given solvent, solutions containing the same number of molecules have the same boiling-point; and, in the same way, in the case of any given solvent, solutions containing the same number of molecules have the same freezing-point. By knowing the weight of the substance dissolved, the weight of the solvent, and the rise in boiling-point caused by the substance, together with certain facts in regard to the solvent, it is possible to draw a conclusion in regard to the molecular weight of the substance. The same is true in regard to the freezing-point. The change effected in this case is a lowering of the freezing-point.

Structural formula. — The formulas $C_2H_6O_2$, $C_2H_4O_2$, C_3H_8, etc., tell us simply the composition of the three compounds represented, and tell us also the relative weights of their molecules. In studying the chemical conduct of these compounds, their decompositions, and the modes of preparing them, we become familiar with many facts which it is desirable to represent by means of the formulas. Thus, for example, but one of the four atoms of hydrogen represented in the formula of acetic acid, $C_2H_4O_2$, can be replaced by metals. It plainly differs from the three remaining atoms, and it is natural to conclude that it is held in the molecule in some way differently from the other three. We may, therefore, write the formula $C_2H_3O_2.H$, which is intended to call attention to the difference. By further study of acetic acid, we find that that particular hydrogen, which gives to it its acid properties, and which, in the above formula, is written by itself, is intimately associated with oxygen. It can be removed with oxygen by very simple reactions, and the place of both taken by one atom of some other element; as, for example, chlorine. Thus, when acetic acid is treated with phosphorus trichloride, PCl_3, it is converted into acetyl chloride, C_2H_3OCl, according to this equation: —

$$3\ C_2H_4O_2 + PCl_3 = 3\ C_2H_3OCl + PO_3H_3.$$

The result of the action is the direct substitution of one atom of chlorine for one atom of hydrogen and one atom of oxygen in acetic acid, a fact which points to an intimate connection between the hydrogen and oxygen in the acid. Further, when acetyl chloride is heated with water, acetic acid is regenerated, hydrogen and oxygen from the water entering into the place occupied by the chlorine, as represented in this equation: —

$$C_2H_3OCl + H_2O = C_2H_4O_2 + HCl.$$

From facts of this kind the conclusion is drawn that in acetic acid hydrogen and oxygen are *connected;* or, as it is said, *linked together;* and this conclusion is represented in chemical language by the formula $C_2H_3O.OH$, which may serve as a simple illustration of what are called *structural* or *constitutional* formulas. In all compounds the attempt is made, by means of a thorough study of the conduct of the compounds, to trace out the connections existing between the constituent atoms. When this can be done for all the atoms contained in a molecule, the *structure* or *constitution* of the molecule or of the compound is said to be determined. The structural formulas which have been determined by proper methods have proved of much value in dealing with chemical reactions, as they enable the chemist who *understands* the language in which they are written to see relations which might easily escape his attention without their aid. In order to *understand* them, however, the student must have a knowledge of the reactions upon which they are based; and he is warned not to accept any chemical formula unless he can see the reasons for accepting it. He should ask the question, *upon what facts is it based?* whenever a formula is presented for the first time. If he does this conscientiously, he will soon be able to use the language intelligently, and the beauty of the relations which exist between the large number of compounds of carbon will be revealed to him. If he does not, his mind will soon be in a hopeless muddle, and what he learns will be

of little value. For the beginner, this advice is of vital importance: *Study with great care the reactions of compounds; study the methods of making them, and the decompositions which they undergo. The formulas are but the condensed expressions of the conclusions which are drawn from the reactions.*

General principle of classification of the compounds of carbon. — In considering the elements and compounds included under the head of Inorganic Chemistry, the fundamental substances are, of course, the elements. The properties of the elements enable us to separate them, for study, into a number of groups; as, for example, the chlorine group, including bromine, iodine, and fluorine; the oxygen group, in which are included sulphur, selenium, and tellurium. To recall the method generally adopted, let us take the chlorine group. In studying the members of this group, there is found great similarity in their properties. Their hydrogen compounds next present themselves, and here the same similarity is met with. Then, in turn, the oxygen and the oxygen and hydrogen compounds are considered, and again the resemblances in properties between the corresponding compounds of chlorine, bromine, and iodine are met with. We thus have groups of elements, and of the derivatives of these elements, as, —

Cl	ClH	ClO_3H
Br	BrH	BrO_3H
I	IH	IO_3H, etc.

Of course, the chlorine group is quite distinct from the oxygen group and from all other groups; and each member of the chlorine group is, at least so far as we know, quite independent of the other members. We cannot make a bromine compound from a chlorine compound, nor a chlorine compound from a bromine compound, without directly substituting the one element for the other.

Now, when we come to study the compounds of carbon, we shall find that the same general principle of classification is

made use of; only, in consequence of the peculiarities of the compounds, the system can be carried out much more perfectly; the members of the same group can be transformed one into the other, and it is also possible to pass from one group to another by means of comparatively simple reactions.

The simplest compounds of carbon are those which contain only hydrogen and carbon, or the *hydrocarbons*. All the other compounds may be regarded as derivatives of the hydrocarbons. To begin with, there are several groups or series of hydrocarbons, which correspond somewhat to the different groups of elements. The members of one and the same series of hydrocarbons resemble one another more closely than the members of one and the same series of elements. Although we have indications of the existence of more than ten series of these hydrocarbons, only three or four of the series are at all well known, and of these, but two include more than two or three members that need to be considered in this book.

Starting with any series of hydrocarbons, several classes of derivatives can be obtained by treating the fundamental compounds with different reagents. The chief classes of these derivatives are: (1) those containing halogens; (2) those containing oxygen, among which are the acids, alcohols, ethers, etc.; (3) those containing sulphur; and (4) those containing nitrogen. Corresponding to every hydrocarbon, then, we may expect to find representatives of these different classes of derivatives. But the relations existing between any hydrocarbon and its derivatives are the same as those existing between any other hydrocarbon and its derivatives. Hence, if we *know* what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon. The student who, for the first time, undertakes the study of the chemistry of the compounds, is apt to feel overwhelmed by the enormous number of compounds described in the book or by the lecturer. This large number is really not a serious matter. No one is expected to become acquainted with every compound. A great

many of these need only be referred to for the purpose of indicating the extent to which the series to which they belong have been developed. In general, the members of any series so closely resemble one another, that, if we understand the simpler members, we have a fair knowledge of the more complicated members.

It is proposed, in this book, to treat only of the more important compounds and the more important reactions, the object being rather to give a clear, general notion of the subject than detailed information regarding particular compounds. Should the student desire more specific information concerning the properties of any of the compounds mentioned, he can easily find it in some larger book. It will, however, hardly be profitable for him, at the outset, to burden his mind with details. He may thereby sacrifice the general view, which it is so important that he should gain as quickly as possible.

The plan which will be followed is briefly this: Of the first series of hydrocarbons *two* members will be treated of. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series, and of other series. Their characteristics and their relations to the hydrocarbons will be dwelt upon, as well as their relations to each other. Thus, by a comparatively close study of two hydrocarbons and their derivatives, we may acquire a knowledge of the principal classes of the compounds of carbon. After these typical derivatives have been discussed, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members.

After the first series has been studied in this way, and a clear idea of the relations between the various classes has been obtained, a second series will be taken up and treated in a similar way, and so on. But, as already stated, only a few of the series require very much attention at the beginning. The first series which will be used for the purpose of illustrating the general principles is one of the *two* most important series, and of the only two that need be taken up at all fully at present.

CHAPTER II.

METHANE AND ETHANE. — HOMOLOGOUS SERIES.

If we were to study all the hydrocarbons known, and were then to arrange them in groups according to their properties, we should find that a large number of them resemble *marsh gas* in their general conduct. Some of the points of resemblance are these: They are very stable, resisting with marked power the action of most reagents; and nothing can be added to them directly, — if any change takes place in them, hydrogen is first given up. On arranging these substances according to the number of carbon atoms contained in them, we have a remarkable series, the first six members of which, together with their formulas, are included in the subjoined table: —

Methane (or Marsh Gas)	CH_4.
Ethane	C_2H_6.
Propane	C_3H_8.
Butane	C_4H_{10}.
Pentane	C_5H_{12}.
Hexane	C_6H_{14}.

On examining the formulas given, we see that the difference in composition between any two consecutive members is represented by CH_2. Thus, adding CH_2 to marsh gas, CH_4, we get ethane, C_2H_6; adding CH_2 to C_2H_6, we get C_3H_8, and so on, in each successive step. Any series of this kind, in which the successive members increase in complexity by CH_2, is called an *homologous series*.

Just as the members of an homologous series of hydrocarbons

differ from one another by CH_2, or some multiple of it, so also the members of any class of derivatives of these hydrocarbons differ from one another in the same way, and form homologous series. Thus, running parallel to the hydrocarbons mentioned above, there are two homologous series of oxygen derivatives, as indicated below: —

$$CH_4 - CH_4O - CH_2O_2.$$
$$C_2H_6 - C_2H_6O - C_2H_4O_2.$$
$$C_3H_8 - C_3H_8O - C_3H_6O_2.$$
$$C_4H_{10} - C_4H_{10}O - C_4H_8O_2.$$
$$C_5H_{12} - C_5H_{12}O - C_5H_{10}O_2.$$
$$C_6H_{14} - C_6H_{14}O - C_6H_{12}O_2.$$

The relation observed between the members of the homologous series mentioned is by no means a peculiarity of the marsh gas series of hydrocarbons and of their derivatives, but is observed in the case of all other series of hydrocarbons and their derivatives.

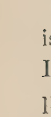
Strictly speaking, there is perhaps no analogy for this remarkable fact among the elements and their compounds, yet facts which suggest analogy are known. Consider, for example, the chlorine series. We have

Chlorine,	with	the	atomic	weight, 35.4
Bromine,	"	"	"	80.
Iodine,	"	"	"	127.

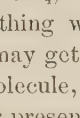
As is well known, the difference between the atomic weights of chlorine and bromine is approximately equal to the difference between those of bromine and iodine. In other words, there is a regular increase in complexity as we pass from chlorine to iodine. Or, at least, there is a regular increase in the atomic weights of these similar elements, just as there is a regular increase in the molecular weights of the similar members of an homologous series. While, however, a satisfactory hypothesis

has been offered to account for the latter fact, and experimental evidence is strongly in favor of the hypothesis, no satisfactory explanation of the former has been offered; or rather no satisfactory experimental evidence has been furnished in favor of the various hypotheses which from time to time have been put forward to account for the similarity between members of the same group of elements.

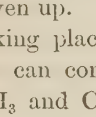
The view at present held in regard to the nature of homology is founded, primarily, upon the idea that carbon is quadrivalent. If carbon is quadrivalent, it of course follows that the compound, marsh gas, CH_4, is saturated; that is, the molecule cannot take up anything without losing hydrogen. In order, therefore, that we may get a compound containing two atoms of carbon in the molecule, some of the hydrogen must first be given up. With our present views, we cannot conceive of union taking place directly between the molecules CH_4 and CH_4, but we can conceive of union taking place between the molecules CH_3 and CH_3, to form a molecule C_2H_6, which in turn is saturated. Representing graphically what is believed to take place, we have, first, marsh gas, which we may represent thus,



If this loses one atom of hydrogen, we have the unsaturated residue



which is capable of uniting with another molecule of the same kind to form the more complex molecule



or C_2H_6, which is believed to express the relation existing between marsh gas, CH_4, and ethane, C_2H_6, or between any two adjoining members of an homologous series. The evidence in favor of this view will be presented when the reactions by means of which the hydrocarbons are made are discussed. The explanation offered, and now generally

accepted, involves the idea that carbon atoms have the power of uniting with each other. And, as the explanation for the relation between the first and second members is, in principle, the same as for the relation between the second and third, the third and fourth, etc., it appears that this power of carbon atoms to unite with one another is very extensive. It is to the power which carbon possesses of forming homologous series, or to the power of the atoms of carbon to unite with each other, that we owe the large number of compounds of this element.

Methane (marsh gas, fire damp), CH_4. — This hydrocarbon is found rising from pools of stagnant water in marshy districts. If a bottle is filled with water and inverted with a funnel in its neck in such a pool, some of the gas can be collected by holding the funnel over the bubbles rising from the bottom. It is also found in large quantities mixed with air, in coal mines, and sometimes issues from the earth, together with other gases, in the neighborhood of petroleum wells.

It can be prepared by treating aluminium carbide, a compound of aluminium and carbon of the formula, C_3Al_4, with water as represented in the equation: —

$$C_3Al_4 + 12\,H_2O = 3\,CH_4 + 4\,Al(OH)_3.$$

This method is of special interest for the reason that it indicates the possibility of making marsh gas from the elements; aluminium carbide and water being made readily from the elements.

It is formed, as its occurrence in marshes indicates, by the decomposition of organic matter under water. In pure condition it is made most readily by mixing 2 parts sodium acetate, 2 parts potassium hydroxide, and 3 parts quicklime, and heating the mixture. Writing sodium instead of potassium hydroxide, the action which takes place is represented thus: —

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

It will be shown hereafter that most acids of carbon break up in a similar way, yielding a hydrocarbon and a carbonate.

Properties. Marsh gas is colorless and inodorous. It is slightly soluble in water, but not so much so as to prevent its collection over water. It burns. Its mixture with air is explosive. It is this mixture which is the cause of the explosions which so frequently take place in coal mines.

Experiment 3. Make marsh gas from dehydrated sodium acetate, potassium hydroxide, and calcium oxide, using the substances in the proportion stated on the preceding page. Dehydrate some sodium acetate by heating it in a porcelain dish on wire gauze over a small flame. Use 10g of sodium acetate. Collect the gas over water. Burn some as it escapes from a jet. In small quantities it does not readily explode with air.

Reagents, in general, do not act readily upon marsh gas. Chlorine in diffused daylight gradually takes the place of the hydrogen, forming a series of compounds which will be treated of under the head of the halogen derivatives of methane. The simplest of them has the composition represented by the formula CH_3Cl, and is known as *chlor-methane* or *methyl chloride*.

Ethane, C_2H_6. — Ethane rises from the earth from some of the gas wells in the regions in which petroleum occurs. It is also found dissolved in crude petroleum.

It can be made from methane by introducing a halogen and making a compound like chlor-methane, CH_3Cl. As the corresponding iodine derivative is less volatile, it is used. This iodomethane, CH_3I, is treated with zinc or sodium in some neutral medium, as, for example, anhydrous ether. The reaction which takes place is represented thus: —

$$CH_3I + CH_3I + 2\ Na = C_2H_6 + 2\ NaI.$$

This method of building up more complex from simpler hydrocarbons has been used extensively; and it is well adapted to showing the relations between the substances formed and the simpler ones from which they are made.

An operation of the kind involved in the above-mentioned

preparation of ethane is called a *synthesis*. The essential feature of the synthesis is the formation of a more complex substance from simpler ones. Our knowledge of the structure of the compounds of carbon is largely dependent upon the use of various methods of synthesis. For example, in the case under consideration, the synthesis gives us at once a clear view of the relations between ethane and methane, and also suggests that homology may be due to similar relations between the successive members of the series,—a view which is fully confirmed by the synthetical preparation of the higher members. A similar method of synthesis has been used in the preparation of tetrathionic acid from sodium thiosulphate. The action is represented thus:—

$$\left.\begin{matrix}Na_2S_2O_3\\Na_2S_2O_3\end{matrix}\right\} + I_2 = \left.\begin{matrix}NaS_2O_3\\NaS_2O_3\end{matrix}\right\rangle + 2\ NaI.$$

Two mol. sodium thiosulphate. Sodium tetrathionate.

CHAPTER III.

HALOGEN DERIVATIVES OF METHANE AND ETHANE.

Substitution. — When methane and chlorine are brought together in diffused daylight, action takes place gradually; hydrochloric acid gas is given off, and one or more products are obtained, according to the length of time the action continues. The products have been studied carefully, and four have been isolated. The composition of these products is represented by the formulas CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. We see thus that the action of chlorine consists in replacing, step by step, the hydrogen of the hydrocarbon. The action is represented by the four equations: —

$$(1)\quad CH_4 + Cl_2 = CH_3Cl + HCl;$$
$$(2)\quad CH_3Cl + Cl_2 = CH_2Cl_2 + HCl;$$
$$(3)\quad CH_2Cl_2 + Cl_2 = CHCl_3 + HCl;$$
$$(4)\quad CHCl_3 + Cl_2 = CCl_4 + HCl.$$

This replacement of hydrogen by chlorine is an example of what is known as *substitution*. We shall find that most hydrocarbons are very susceptible to the influence of the halogens and a number of other reagents, such as nitric acid, sulphuric acid, etc., and that thus a large number of derivatives can be made, differing from the hydrocarbons in that they contain one or more halogen atoms or complex groups in the place of the same number of hydrogen atoms. It must be borne in mind that the mere fact that chlorine, in acting upon marsh gas, is substituted for an equivalent quantity of hydrogen, does not prove that

the chlorine in the product occupies the same place that the replaced hydrogen did. Nevertheless, a careful study of all the facts regarding the products thus formed has led to the belief that the substituting atom or residue does occupy the same place, or bear the same relation to the carbon atom as the hydrogen did.

The name *substitution-products* properly includes all products made from the hydrocarbons, or from other carbon compounds, by the substitution process. The principal ones are those formed by the action of the halogens, or the *halogen substitution-products;* those formed by the action of nitric acid, or the *nitro-substitution-products;* and those formed by the action of sulphuric acid, or the *sulphonic acids.* The last are, however, not commonly called substitution-products.

Chlor-methane, methyl chloride, CH_3Cl.
Brom-methane, methyl bromide, CH_3Br.
Iodo-methane, methyl iodide, CH_3I.

The chlorine and bromine products can be made by treating methane with the corresponding element. They can be most easily made by treating methyl alcohol with the corresponding hydrogen acids: —

$$\underset{\text{Methyl alcohol.}}{CH_4O} + HCl = \underset{\text{Chlor-methane.}}{CH_3Cl} + H_2O.$$

Di-iodo-methane, methylene iodide, CH_2I_2. — This substance is the principal halogen derivative of methane containing two halogen atoms. It is made from iodoform or tri-iodo-methane, CHI_3, by treating it with hydriodic acid, the latter acting as a reducing agent: —

$$CHI_3 + HI = CH_2I_2 + I_2.$$

As will be seen, this is a case of *reverse substitution;* in other words, the action is the opposite of that described above as substitution. Methylene iodide is a liquid that boils at 180° and has the specific gravity 3.342.

Chloroform, $CHCl_3$.
Bromoform, $CHBr_3$.
Iodoform, CHI_3.

The best known and most extensively used of these three derivatives is *chloroform* or tri-chlor-methane. It is made by treating alcohol or acetone with "bleaching powder." The action is deep-seated, involving at least three different stages. It will be treated of more fully under the head of chloral (which see). Chloroform is a heavy liquid of specific gravity 1.526. It has an ethereal odor, and a somewhat sweet taste. It is scarcely soluble in water. It boils at 62°. It is one of the most valuable anæsthetics, though there is some danger attending its use.

Experiment 4. Mix 550g bleaching powder and 1¼ litres water in a 3-litre flask. Add 33g alcohol of sp. gr. 0.834. Heat gently on a water-bath until action begins. A mixture of alcohol, water, and chloroform will distil over. Add water, and remove the chloroform by means of a pipette. Add calcium chloride to the chloroform, and, after standing, distil on a water-bath.

Iodoform, which is used extensively in surgery, is made by bringing together alcohol, an alkali, and iodine. It is a solid substance, soluble in alcohol and ether, but insoluble in water. It crystallizes in delicate, six-sided, yellow plates. Melting-point, 119°.

Experiment 5. Dissolve 20g crystallized sodium carbonate in 100g water. Pour 10g alcohol into the solution, and, after heating to 60° to 80°, gradually add 10g iodine. The iodoform separates from the solution.

Tetra-chlor-methane, CCl_4, is made by treating carbon disulphide with chlorine, and by treating chloroform with iodine chloride, ICl.

Equivalence of the hydrogen atoms in methane. Having thus seen that the hydrogen atoms of methane can easily be replaced, the interesting question suggests itself whether these hydrogen atoms all bear the same relation to the carbon atom. We accept the conclusion that the carbon atom is quadrivalent,

and that each of the four hydrogen atoms is in combination with it, as indicated in the formula (4) $H-\overset{\overset{H(1)}{|}}{\underset{\underset{H(3)}{|}}{C}}-H(2)$. Do the atoms numbered 1, 2, 3, and 4 bear the same relation to the carbon or not? If they do not, then, on replacing H (1) by chlorine, the product should be different from that obtained by replacing H (2), H (3), or H (4); or, it should be possible to make more than one variety of chlor-methane and of similar products. This subject is an extremely difficult one to deal with. It can only be said that, although chlor-methane has been made in several ways, the product obtained is always the same one; and the same is true of all other substitution products of methane. *Hence, we have no reason whatever for believing that there are any differences between the hydrogen atoms of methane. We therefore conclude that they all bear the same relation to the carbon atom.*

This conclusion is of fundamental importance in dealing with the higher members of the methane series, and, indeed, in dealing with all carbon compounds, as will be seen later.

Chlor-ethane, ethyl chloride, C_2H_5Cl.
Brom-ethane, ethyl bromide, C_2H_5Br.
Iodo-ethane, ethyl iodide, C_2H_5I.

These substances are all liquids having pleasant ethereal odors. The first boils at 12°, the second at 38.8°, and the third at 72°. They are most readily made from alcohol, by treating with the corresponding hydrogen acids. In the case of the bromide and iodide, it is simpler to treat the alcohol with red phosphorus and the halogen. The action is similar to that involved in making hydrobromic acid by treating water with red phosphorus and bromine. It will be shown that alcohol is a hydroxide, in which hydroxyl (OH) is in combination with the group C_2H_5, called ethyl, as represented in the formula $C_2H_5.OH$. When

bromine is brought in contact with red phosphorus, the tribromide, PBr_3, is formed, and this acts upon the alcohol thus: —

$$\left.\begin{array}{l} C_2H_5.OH \quad Br \\ C_2H_5.OH + Br \\ C_2H_5.OH \quad Br \end{array}\right\} P = 3\ C_2H_5Br + P(OH)_3.$$

When water is used instead of alcohol, the bromine appears in combination with hydrogen as hydrobromic acid.

Experiment 6. Arrange an apparatus as represented in Fig. 4.

In the flask place 10g red phosphorus and 60g absolute alcohol. Put 60g bromine in the glass-stoppered funnel, and, by means of the stop-

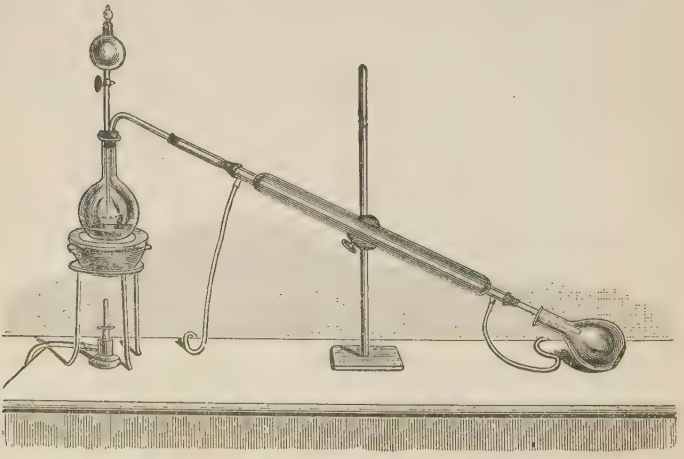


Fig. 4.

cock, let the bromine enter the flask very slowly, drop by drop. After allowing the mixture to stand for two or three hours, gently heat the water-bath, and the brom-ethane will distil over. Place the distillate in a glass-stoppered cylinder, and shake it first with water to which some caustic soda has been added, and then two or three times with water alone. Separate the water from the brom-ethane either by means of a pipette[1] or a separating funnel. Add two or three pieces of fused

[1] A good pipette for separating two liquids of different specific gravities can be easily made as follows: Select a piece of glass tubing about 1.5 to 2cm internal diameter, and a

calcium chloride the size of a small marble, and let stand for a few hours. Then pour off into a clean, dry distilling bulb, and distil, noting the boiling-point.

Among the many halogen substitution-products of ethane containing more than one halogen atom, only two will be mentioned. These are the two *di-chlor-ethanes*, both of which are represented by the formula $C_2H_4Cl_2$. The existence of these two substances, having the same composition but entirely different properties, affords a good example of what is known as *isomerism.*

Isomerism. — One of the most striking and interesting facts with which we become familiar in studying carbon compounds, is the frequent occurrence of two, and often more, substances containing the same elements in the same proportions by weight. Substances which bear this relation to one another are said to be *isomeric.*

Isomerism is of two kinds: (1) Substances may have the same percentage composition and the same molecular weights. Such bodies are said to be *metameric.* The di-chlor-ethanes, $C_2H_4Cl_2$, for example, are metameric. (2) Substances which have the same percentage composition but different molecular weights are said to be *polymeric.* Acetylene, C_2H_2, benzene, C_6H_6, and styrene, C_8H_8, are polymeric.

second that will fit snugly into it, so that it can be moved up and down without difficulty. Draw out the larger tube, and fit to it a tube of about 6^{mm} diameter and 16^{cm} long. Then draw out this last tube to a small opening. Close the smaller of the two large tubes by melting it together. Finally, put this tube into the largest one, and draw over the two a broad piece of thick rubber tubing, which will close the opening between the two, and at the same time permit the upward and downward movement of the smaller tube. The pipette has the form represented in Fig. 5.

Fig. 5.

The dimensions may be varied, but the following will be found convenient: length of widest tube about 16 to 20^{cm}; total length of inner tube, or piston, about 25 to 30^{cm}. Instead of drawing the large tube out and fitting the smaller tube to it, the union may be made by means of a cork.

The cause of isomerism is undoubtedly to be found in the different relations which the parts of isomeric compounds bear to each other. Our structural formulas, which show the relations between the parts of compounds which have been traced out by a study of the chemical conduct of these compounds, give us an insight into the causes of isomerism. To illustrate, let us take the two di-chlor-ethanes. One of these is made by treating ethane, the other by treating ethylene, C_2H_4, with chlorine. In the first case the action is substitution; in the second, the chlorine is added directly to ethylene, thus, —

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

The product from ethylene is called *ethylene chloride;* that from ethane, *ethylidene chloride.* It will be shown that ethylene is to be represented by the formula $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$; that is, that in it two hydrogen atoms are in combination with each of the carbon atoms. Now, if chlorine is brought in contact with this substance, we should naturally expect each of the carbon atoms to take up one atom of chlorine, and thus to become saturated, as represented in the equation, —

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \quad \begin{matrix} Cl \\ + \\ Cl \end{matrix} \quad = \begin{matrix} CH_2Cl \\ | \\ CH_2Cl. \end{matrix}$$

Chlorine is taken up, and it is believed that the ethylene chloride obtained has the structure represented by the formula $\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$, the distinctive feature of which is that each of the chlorine atoms is in combination with a different carbon atom.

We, however, can conceive of another possibility; viz., that the chlorine atoms are both in combination with the same carbon atom, as represented in the formula $\begin{matrix} CHCl_2 \\ | \\ CH_3 \end{matrix}$, and we should be inclined to the view that this represents the structure

of ethylidene chloride. Fortunately we have experimental evidence to support this view. It will be shown that aldehyde has the formula $\begin{matrix}\text{CHO}\\|\\\text{CH}_3\end{matrix}$. When aldehyde is treated with phosphorus pentachloride, two chlorine atoms take the place of the oxygen. A product which must be represented by the formula $\begin{matrix}\text{CHCl}_2\\|\\\text{CH}_3\end{matrix}$ is formed, and this is identical with ethylidene chloride. Thus it will be seen that the difference between the two isomeric compounds, ethylene chloride and ethylidene chloride, depends upon the fact that in the former the two chlorine atoms are in combination with different carbon atoms, while in the latter both chlorine atoms are in combination with the same carbon atom.

General characteristics of the halogen derivatives of methane and ethane. The one characteristic to which it is desirable that special attention should be called is the condition of the halogens in the compounds. In general, chlorine in combination in organic compounds can be detected by means of silver nitrate, or when dissolved in water, these compounds are ionized. The halogen substitution products of the hydrocarbons are not ionized by water, and the chlorine in them cannot be detected by means of silver nitrate in the ordinary way. On the other hand, when chlor-methane is heated with a silver compound, the chlorine is removed. Sodium and zinc have the power of extracting the chlorine, bromine, etc., from halogen derivatives, and this fact is taken advantage of in the synthesis of many hydrocarbons. (See "Ethane," p. 24.)

CHAPTER IV.

OXYGEN DERIVATIVES OF METHANE AND ETHANE.

There are several classes of oxygen derivatives of the hydrocarbons. Among them are the important compounds known as alcohols, ethers, aldehydes, and acids. Each of these classes will be taken up in turn.

1. Alcohols.

Among the most important oxygen derivatives are the alcohols, of which methyl alcohol, or wood spirits, and ethyl alcohol, or spirits of wine, are the best known examples. As far as composition is concerned, these bodies bear very simple relations to the two hydrocarbons, methane and ethane. These relations are indicated by the formulas, —

Hydrocarbons.	Alcohols.
CH_4	CH_4O
C_2H_6	C_2H_6O.

The molecule of the alcohol differs from that of the corresponding hydrocarbon by one atom of oxygen. In order to understand the chemical nature of alcohols, it will be best to study with some care the reactions of one; and we may take for this purpose the simplest one of the series, methyl alcohol.

Methyl alcohol, Methanol, CH_4O. — This alcohol is also known as wood spirits. It is found in nature in combination in the oil of wintergreen. It is formed, together with many other substances, in the dry distillation of wood. It is hence contained in crude pyroligneous acid or wood vinegar. Wood is distilled in large quantities for various purposes; chiefly, however, for

making charcoal. In some charcoal factories the distillate is collected and utilized. Wood is distilled also for the purpose of making vinegar, or pure acetic acid.

It is not an easy matter to get pure methyl alcohol from crude wood spirits. Fractional distillation alone will not answer; though, if the mixture is distilled for some time, and the impure alcohol thus obtained then converted into some crystalline derivative, the latter can be purified and then decomposed in such a way as to yield the alcohol in pure condition.

Methyl alcohol is a liquid that boils at 66.7°, and has the specific gravity 0.8142 at 0°. It closely resembles ordinary alcohol in all its properties. It burns with a non-luminous flame. When taken into the system it intoxicates. In concentrated form it is poisonous. It is an excellent solvent for fats, oils, resins, etc., and is extensively used for this purpose.

1. *Action of hydrochloric, hydrobromic, and other acids on methyl alcohol.* The action of a few acids is represented by the following equations: —

$$CH_4O + HBr = CH_3Br + H_2O;$$
$$CH_4O + HCl = CH_3Cl + H_2O;$$
$$CH_4O + HNO_3 = CH_3NO_3 + H_2O;$$
$$CH_4O + H_2SO_4 = CH_3.HSO_4 + H_2O.$$

The action is plainly suggestive of that of metallic hydroxides or bases. In each case, except the last, the acid is neutralized and water is formed, just as the acid would be neutralized by potassium hydroxide.

2. *Action of phosphorus trichloride.* When phosphorus trichloride acts on methyl alcohol, the products are chlor-methane and phosphorous acid: —

$$3\ CH_4O + PCl_3 = 3\ CH_3Cl + P(OH)_3.$$

Here one atom of chlorine is substituted for an atom of hydrogen, the reaction being like that which takes place between water and phosphorus trichloride: —

$$3\ H_2O + PCl_3 = 3\ HCl + P(OH)_3.$$

This fact would lead us to suspect that there is some resemblance between the alcohol and water.

3. *Action of potassium and sodium.* When potassium is brought in contact with pure methyl alcohol, hydrogen is given off, and a compound containing potassium is formed: —

$$CH_4O + K = CH_3KO + H.$$

Further treatment of this compound with potassium causes no further evolution of hydrogen, so that plainly one of the four hydrogen atoms contained in methyl alcohol differs from the other three.

The resemblance between methyl alcohol and metallic hydroxides; the substitution of chlorine for hydrogen and oxygen; and the resemblance between the alcohol and water; and, finally, the substitution of potassium for one, and only one, hydrogen atom, lead to the conclusion that the alcohol contains hydrogen and oxygen in combination, and that the characteristic reactions are due to the presence of the group called *hydroxyl* (OH). The analogy between the alcohol, a metallic hydroxide, and water is shown by these formulas: alcohol, $CH_3.OH$; hydroxide, K.OH; water, H.OH. Thus water appears as the type of both the hydroxide and the alcohol, and they may be regarded as derived from water by substituting the group CH_3 for one hydrogen atom in the case of the alcohol, and substituting an atom of the metal potassium for one hydrogen atom in the case of the hydroxide. Or, on the other hand, methyl alcohol may be regarded as marsh gas in which one of the hydrogen atoms is replaced by hydroxyl. The two views are in fact identical.

To test the correctness of the view, we may try to make methyl alcohol in some way that will show us of what parts it is made up. Thus, we may start with marsh gas, and introduce a halogen, as bromine. Now, if we bring brom-methane together with a metallic hydroxide, the bromine and the metal may unite, leaving the hydroxyl and the group CH_3, which may unite also, as indicated in the equation

$$CH_3Br + MOH = CH_3.OH + MBr.$$

If methyl alcohol could be made in this way, we should have very clear proof of the correctness of the view expressed in the formula $CH_3.OH$. Methyl alcohol has been made by this reaction; and it is indeed a general reaction for the preparation of alcohols, so that the proof that alcohols are hydroxides is conclusive.

The reactions above presented show that the part of methyl alcohol that corresponds to the metal in the hydroxide is the group CH_3. This it is which enters into the acids in place of their hydrogen, and this remains unchanged when potassium acts upon the alcohol. It has received the name *methyl*. Hence we have the names methyl alcohol, methyl bromide, methyl ether, etc. A group which, like methyl, appears in a number of compounds is called a *radical*, or *residue*. These names are intended simply to designate that part of a carbon compound which remains unchanged when the compound is subjected to various transforming influences.

The two most characteristic reactions of methyl alcohol are: (1) its power to form salt-like compounds when treated with acids; and (2) its power to form an acid when oxidized.

The neutral compounds formed with acids correspond to the salts of metals, only they contain the radical, or residue, methyl, CH_3, in the place of metals. They are called *ethereal salts*, or *esters*.

The acid formed by oxidation has the composition expressed by the formula CH_2O_2. It contains one atom of oxygen more and two atoms of hydrogen less than the alcohol from which it is formed. It will be shown that this acid is the first of an important series of acids, known as the *fatty acids*, each of which bears the same relation to a hydrocarbon containing the same number of carbon atoms that this simplest acid bears to marsh gas.

Ethyl alcohol, Ethanol, $C_2H_5.OH$. — This is the best known substance belonging to the class of alcohols. It is known also by the name *spirits of wine* and *ordinary alcohol*. It occurs in small quantities widely distributed in nature.

The one method of preparation upon which we are dependent for alcohol is the fermentation of sugar.

Fermentation. — Whenever a plant juice which contains sugar is left exposed to the air, it gradually undergoes a change by which it loses its sweet taste. Usually the change consists in a breaking up of the sugar into carbon dioxide and alcohol. The equation

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = 2\ \underset{\text{Alcohol.}}{C_2H_6O} + 2\ CO_2,$$

approximately expresses what takes place in the process which is known as *alcoholic fermentation*. It has been shown that fermentation is caused by the presence of small organized bodies, either animal or vegetable. These bodies, which are known as *ferments*, are of different kinds, and cause different kinds of fermentation with different products. Among the kinds of fermentation the following may be specially mentioned: —

1. *Alcoholic* or *vinous fermentation*. This is caused by a vegetable ferment which is contained in ordinary yeast. The ferment consists of small, round cells arranged in chains. The products of its action are alcohol and carbon dioxide.

2. *Lactic acid fermentation*. This is due to a vegetable ferment which is contained in sour milk. It has the power of transforming sugar into lactic acid.

3. *Acetic acid fermentation*. This is due to a peculiar vegetable ferment which acts upon alcohol, transforming it into acetic acid.

The germs of various ferments are in the air; and, whenever they find favorable conditions, they develop and produce their characteristic effects. They will not develop in a solution of pure sugar. The variety of sugar which is fermentable, and which is the one from which alcohol is obtained, is not our ordinary cane sugar, but one known as *grape sugar;* or, more commonly, *glucose*. In order that the ferments may grow, there

must be present in the solution, besides the sugar, substances which contain nitrogen. These, as well as the sugar, are contained in the juices pressed out from fruits, and hence these juices readily undergo fermentation.

In the manufacture of alcohol a solution containing sugar is first prepared from the residue of wine presses, or from some kind of grain or potatoes. In case the solution contains grape sugar, this undergoes fermentation directly when the ferment is added. If the substance in solution is cane sugar, this is first changed by the ferment into grape sugar and fruit sugar, and the fermentation then takes place as in the first case.

Experiment 7. Dissolve about 150^{g} commercial grape sugar in 1 to 1½ litres of water in a good-sized flask. Connect the flask by means of a bent tube with a cylinder containing clear lime water. Protect the latter from the air by means of a tube containing caustic potash. Now add to the solution of grape sugar a little brewer's yeast; close the connections, and allow to stand. Soon an evolution of gas will begin, and, as this passes through the lime water, a precipitate of calcium carbonate will be formed. After the action is over, place the flask in a water-bath; connect with a condenser, and distil over 100^{cc} of the liquid. Examine this for alcohol.

A good way to detect alcohol is this: Warm the solution to be tested; add a small piece of iodine and then caustic potash until the color is destroyed. On cooling, a yellow crystalline powder of *iodoform* is deposited.

To obtain alcohol from fermented liquids, these must be distilled. The ordinary alcohol contains water, and a mixture of other alcohols called *fusel oil*. The latter can be removed partly by distillation, and the last portions can be got rid of by filtering through charcoal. The water cannot be removed completely by distillation, though a product containing about 96 per cent of alcohol can be obtained in this way.

Absolute alcohol is ordinary alcohol from which the water has been removed to a considerable extent by means of some dehydrating agent, as quicklime, barium oxide, or anhydrous copper

sulphate. By continued treatment with lime the quantity of water can be reduced to one-half a per cent, and this small quantity can be removed by treatment with metallic sodium.

Experiment 8. Prepare absolute alcohol from ordinary strong alcohol. For this purpose a good-sized flask is one-half to two-thirds filled with quicklime broken into small lumps. The alcohol is poured upon the lime, and allowed to stand at least twenty-four hours, when it is distilled off on a water-bath. If the alcohol used contains considerable water, it is necessary to repeat the treatment with lime.

Pure ethyl alcohol has a peculiar, pleasant odor. It is claimed, however, that perfectly anhydrous alcohol has no odor. It remains liquid at very low temperatures, but has recently been converted into a solid at a temperature of $-130.5°$. It boils at 78.3°. It burns with a non-luminous flame, which does not leave a deposit of soot on substances placed in it. It is hence used for heating purposes. When mixed with air its vapor explodes when a flame is applied. Its effects upon the human system are well known. It intoxicates when taken in dilute form, while in concentrated form it is poisonous. When taken internally in large doses, it lowers the temperature of the body from 0.5° to 2°, although the sensation of warmth is experienced.

Alcohol is the principal solvent for substances of organic origin. It is hence extensively used in the arts, as in the manufacture of varnishes, perfumes, and tinctures of drugs.

The many beverages which are in use depend for their efficiency upon the presence of alcohol in greater or smaller quantity. The milder forms of beer contain from 2 to 3 per cent; light wines, such as claret, about 8 per cent; while whiskey, brandy, rum, and other distilled liquors sometimes contain as much as 60 to 75 per cent. These distilled liquors are nothing but ordinary alcohol with water and small quantities of substances obtained from the fruit or grain used in their preparation, or obtained by standing in barrels made of oak wood. The different flavors are due to the small quantities of these substances.

Chemical conduct of ethyl alcohol. All that was said in regard to the chemical conduct of methyl alcohol applies to ethyl alcohol. The action of acids, of phosphorus trichloride, of the alkali metals, and of oxidizing agents is the same as in the case of methyl alcohol, only the products formed contain the radical, ethyl, C_2H_5, instead of methyl.

NOTE FOR STUDENT. — The student is advised to write the equations representing the action of hydrochloric, hydrobromic, and nitric acids; of phosphorus trichloride; and of potassium, upon ethyl alcohol. What is the composition of the acid formed by oxidation of ordinary alcohol?

2. ETHERS.

As has been shown, when an alcohol is treated with potassium or sodium, compounds are formed having the formulas

$$CH_3ONa,\ CH_3OK,\ C_2H_5OK,\ C_2H_5ONa.$$

If one of these is treated with a mono-halogen derivative of a hydrocarbon, as, for example, iodo-methane, CH_3I, reaction takes place thus: —

$$CH_3ONa + CH_3I = C_2H_6O + NaI.$$

These reactions leave very little room for doubt in regard to the structure of the compound C_2H_6O. It must be represented by the formula $CH_3 - O - CH_3$, or $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O$, or $(CH_3)_2O$. Comparing it with methyl alcohol, we see that it is obtained from the alcohol by replacing the hydrogen of the hydroxyl by methyl, CH_3. Just as the alcohol is analogous to the hydroxide KOH, so the new compound is analogous to the oxide K_2O. It is the representative of a class of bodies known as *ethers*, which are analogous to the oxides of the metals. Our ordinary ether is the chief representative of the class.

While the reaction above mentioned serves admirably to show the relations between the alcohols and ethers, it is not the one

that is made use of in their preparation. This consists in treating the alcohols with sulphuric acid, and distilling.

Ethyl ether, $C_4H_{10}O = (C_2H_5)_2O$. — This is the substance commonly known simply as *ether*, or *sulphuric ether*. The latter name was originally given to it because sulphuric acid is used in its manufacture, and plainly not because any sulphur is contained in it. Ether can be made from alcohol by making the sodium compound of alcohol, C_2H_5ONa, and heating this with brom- or iodo-ethane thus: —

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI;$$

or by converting the alcohol into ethyl iodide and heating this with silver oxide: —

$$2\,C_2H_5I + Ag_2O = (C_2H_5)_2O + 2\,AgI.$$

Practically, however, ether can be made much more readily, and it is made on the large scale by mixing sulphuric acid and alcohol in certain proportions, and then distilling the mixture as described below. Two distinct reactions are involved in this process. First, when alcohol and sulphuric acid are brought together, half the hydrogen of the acid is replaced by ethyl, thus: —

$$C_2H_5OH + \left.\begin{matrix}H\\H\end{matrix}\right\rangle SO_4 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle SO_4 + H_2O.$$

The product formed is called *ethyl-sulphuric acid*.

Experiment 9. Slowly pour 20 to 30^{cc} concentrated sulphuric acid into about the same volume of alcohol of 80 to 90 per cent. Stir thoroughly, and dilute with a litre of water. In an evaporating dish add powdered barium carbonate until the liquid is neutral. Filter, and examine the clear filtrate for barium. Its presence shows that a soluble barium salt has been formed. This is barium ethyl-sulphate, $Ba(C_2H_5SO_4)_2$.

When ethyl-sulphuric acid is heated with alcohol, ether is formed, and sulphuric acid is regenerated thus: —

$$C_2H_5OH + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle SO_4 = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + H_2SO_4.$$

The ether thus formed distils over; and, if alcohol is admitted

to the sulphuric acid, ethyl-sulphuric acid will again be formed, and with excess of alcohol it will yield ether. The actual method of procedure is described in

Experiment 10. Arrange an apparatus as shown in Fig. 6. As ether is very volatile and inflammable, it is important that the condenser be connected with the receiver by means of an adapter, and the receiver placed in a vessel containing ice ; or a towel may be wrapped around the neck of the receiver and the condensing tube. In the flask put a mixture of 200^g alcohol, and 360^g ordinary concentrated sulphuric acid. It is better to mix them in another vessel, and allow the mixture to stand for some time until it is thoroughly

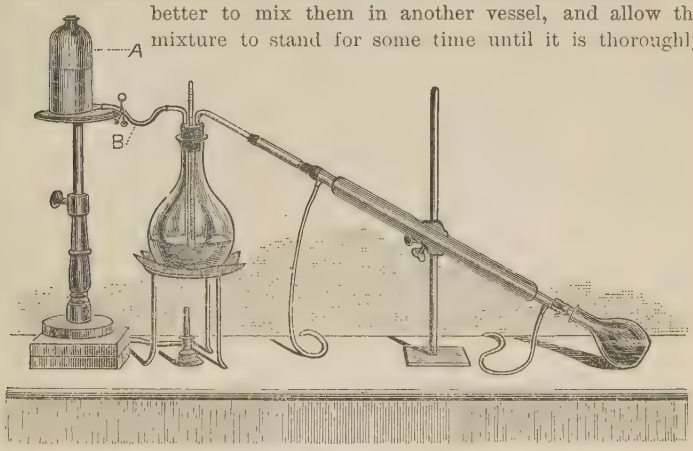


Fig. 6.

cooled down; and then to pour off from any deposited solid as completely as possible. Now heat until the thermometer indicates the temperature 140°. At this point the mixture boils, and ether begins to pass over. As soon as this is noticed, open the stop-cock of the vessel *A*, and let a slow stream of alcohol pass into the distilling flask through the tube *B*, which must reach beneath the surface of the mixture. Regulate this stream so that the temperature remains as near 140° as possible. In this way the operation can be kept up for a considerable time, the alcohol admitted to the flask passing out as ether, and being collected together with some alcohol in the receiver. After about a half litre to a litre of distillate has been collected, stop the operation. The mixture in the distilling flask can be kept in a stoppered bottle and used again when needed. Pour the distillate into a glass-stoppered

cylinder, and add water. The ether will rise to the top, forming a distinct layer, and can be removed by means of a pipette or separating funnel. It should be shaken in this way a few times with water; then treated with a little calcium chloride; and, after standing, poured off into a dry flask, and distilled on a water-bath.

N.B. *Never boil ether over a free flame; and, in working with it, always carefully avoid the neighborhood of flames. In boiling it on a water-bath, do not heat the water to boiling.*

Ether is a colorless, mobile liquid of a peculiar odor and taste. It boils at 34.9°. (Hence the necessity for the precautions mentioned above.) Its specific gravity is 0.736 at 0°. (What evidence have you had that it is lighter than water?) It is very inflammable.

Experiment 11. Put a few cubic centimetres of ether in a small evaporating dish, and apply a flame.

When its vapor is mixed with air, the mixture is extremely explosive. Ether is somewhat soluble in water, and water is also somewhat, though less, soluble in ether; so that when the two are shaken together the volume of the ether becomes smaller, even though every precaution is taken to avoid evaporation. Ether mixes with alcohol in all proportions. It is a good solvent for resins, fats, alkaloids, and many other classes of carbon compounds.

It is an excellent anæsthetic, and is used extensively in this capacity. In consequence of its rapid evaporation, it is used to produce cold, as in the manufacture of ice. So, also, when brought against the skin in the form of spray, the cold produced is so great as to cause insensibility.

Experiment 12. In a thin glass test-tube put 5^{cc} water. Introduce the tube into a small beaker containing some ether. Force air over the surface of the ether by means of a bellows. The water will be frozen.

Chemical conduct of ether. If we were dependent upon the decompositions and general reactions of ether for our knowledge of its structure, we should be left in grave doubt as to the rela-

tions existing between it and alcohol. Its decompositions are mostly deep-seated, and not easily explained. Fortunately, as we have seen, its synthesis from sodium ethylate, C_2H_5ONa, and iodo-ethane, C_2H_5I, leaves us in no doubt regarding its structure. The simplest decompositions are these: —

Heated with acidified water to 150° in a sealed tube, it is converted into alcohol: —

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O + \begin{matrix} H \\ H \end{matrix} > O = 2\ C_2H_5OH.$$

Treated with hydriodic acid at a low temperature, alcohol and iodo-ethane are formed: —

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O + \begin{matrix} H \\ I \end{matrix} = C_2H_5OH + C_2H_5I.$$

Mixed ethers. — Just as ordinary or ethyl alcohol yields ethyl ether, so methyl alcohol yields methyl ether, $(CH_3)_2O$. By modifying the method, a *mixed ether*, *methyl-ethyl ether*, $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O$, can be obtained. This is formed by treating sodium methylate with iodo-ethane, or by treating sodium ethylate with iodo-methane: —

$$CH_3ONa + C_2H_5I = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O + NaI;$$

$$C_2H_5ONa + CH_3I = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O + NaI.$$

It is formed also by distilling methyl alcohol with ethyl-sulphuric acid, or ethyl alcohol with methyl-sulphuric acid: —

$$\begin{matrix} CH_3 \\ H \end{matrix} > O + \begin{matrix} C_2H_5 \\ H \end{matrix} > SO_4 = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O + H_2SO_4;$$

$$\begin{matrix} C_2H_5 \\ H \end{matrix} > O + \begin{matrix} CH_3 \\ H \end{matrix} > SO_4 = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O + H_2SO_4.$$

Methyl ether and methyl-ethyl ether are very similar to ordinary ether.

3. Aldehydes.

It has been stated above that when methyl and ethyl alcohols are oxidized, they are converted into acids having the formulas CH_2O_2 and $C_2H_4O_2$, respectively. By proper precautions, products can be obtained intermediate between the alcohols and acids, and differing from them in composition in that they contain two atoms of hydrogen less than the corresponding alcohols. These products are called *aldehydes*, from *alcohol dehydrogenatum*, from the fact that they must be regarded as alcohols from which hydrogen has been abstracted. The relations in composition between the hydrocarbons, alcohols, and aldehydes are shown by these formulas:—

Hydrocarbons	Alcohols.	Aldehydes.
CH_4	CH_4O	CH_2O
C_2H_6	C_2H_6O	C_2H_4O
etc.	etc.	etc.

Formic aldehyde, Formal, Methanal, CH_2O.—This aldehyde is made by passing the vapor of methyl alcohol together with air over a heated platinum or copper spiral. When cooled to a low temperature it forms a liquid that boils at $-21°$. It is manufactured on the large scale, and comes into the market in solution under the name of *formalin*. It is used in the manufacture of some dyes and as a preservative and disinfectant. When its solution in water is evaporated, a solid substance having the same composition as formic aldehyde is obtained. This is no doubt a polymeric variety, and it may be represented by the formula $(CH_2O)n$. It is called *paraformaldehyde*.

In order to gain a clear insight into the nature of the aldehydes, it will be best to study the best-known representative of the class, which is acetic aldehyde.

Acetic aldehyde, Ethanal, C_2H_4O.—This aldehyde is formed whenever alcohol is brought in contact with an oxidizing

mixture; as, for example, potassium dichromate and dilute sulphuric acid.

Experiment 13. Dissolve a little potassium dichromate in water, and add sulphuric acid. Now add a few cubic centimetres of alcohol, and notice the odor which is that of aldehyde. Notice, also, the change of color of the solution, showing the reduction of the chromate.

As aldehyde is a very volatile liquid, it is difficult to collect it. In preparing it, it is therefore best to pass it into some liquid which will absorb it, and then afterwards separate it by some appropriate method. A good method is that described below.

Experiment 14. Arrange an apparatus as shown in Fig. 7. Put 120^{g} granulated potassium dichromate in the flask *A*, which must have a capacity of 1½ to 2 litres. Make a mixture of 160^{g} concentrated sul-

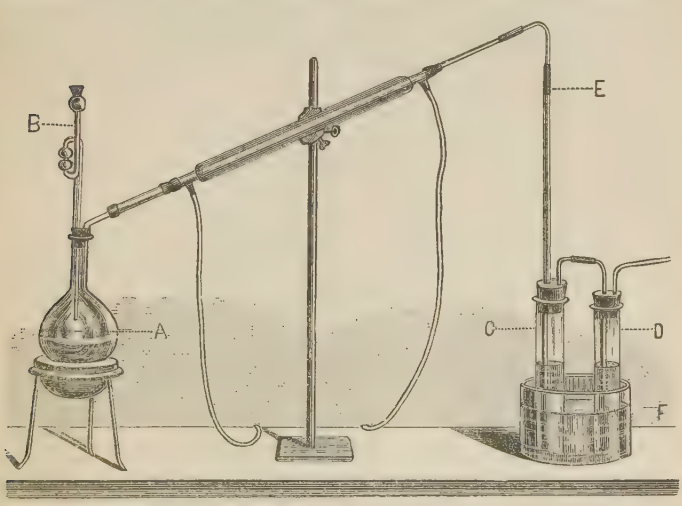


Fig. 7.

phuric acid, 480^{g} water, and 120^{g} alcohol. Cool the mixture down to the ordinary temperature, and then pour it *slowly* through the funnel-tube *B* into the flask, which should stand on a water-bath containing

warm water. The cylinders *C* and *D* are about half filled with ordinary ether, each one containing about 200cc ether, and placed in the large vessel *F*, which contains ice water. The condenser should be supplied with water of about 30° C.

Usually, when the alcohol, water, and sulphuric acid are poured upon the dichromate, the action begins without application of heat. At times it takes place rapidly, so that the liquid should always be added slowly. The aldehyde which is thus formed, together with some alcohol and water vapor, passes into the condenser-tube, where the greater part of the alcohol and water is condensed and returned to the flask, while the aldehyde, being much more volatile, passes into the ether and is there absorbed. After the action is over, the distilling vessel and condenser are removed, and, at *E*, connection is made with an apparatus furnishing *dry* ammonia gas. The gas is passed into the cold ethereal solution of aldehyde to the point of saturation. A beautifully crystallized compound of aldehyde and ammonia, known as *aldehyde-ammonia*, is deposited. The ether is poured off, and the crystals placed on filter-paper. They gradually undergo change in the air, becoming yellow, and acquiring a peculiar odor. If the crystals are placed in a flask and treated with dilute sulphuric acid, pure aldehyde passes over, and can be condensed by ice-cold water.

In the process of purification of ordinary alcohol it is filtered through charcoal. It is thus partly oxidized to aldehyde; and, when it is afterwards distilled, the first portions that pass over contain aldehyde, which was formerly obtained on the large scale by repeated distillation of these "first runnings."

Aldehyde is a colorless liquid, boiling at 21°. It mixes with water and alcohol in all proportions. Its odor is marked and characteristic.

From the chemical point of view, the most characteristic property of aldehyde is its power to unite directly with other substances. It unites with oxygen to form acetic acid; with hydrogen to form alcohol; with ammonia to form *aldehyde-ammonia*, $C_2H_4O.NH_3$; with hydrocyanic acid to form *aldehyde hydrocyanide*, $C_2H_4O.HCN$; with the acid sulphites of the alkalies forming compounds represented by the formulas $C_2H_4O.HKSO_3$ and $C_2H_4O.HNaSO_3$; and with other substances. Indeed, if left to itself, it readily changes into polymeric modi-

fications, uniting with itself to form more complex compounds, *paraldehyde* and *metaldehyde*.

Paraldehyde, $C_6H_{12}O_3$. — This is formed by adding a few drops of concentrated sulphuric acid to aldehyde, which causes the liquid to become hot. On cooling to 0°, the paraldehyde solidifies in crystalline form. It melts at 10.5°. It dissolves in eight times its own volume of water, and boils at 124°. When distilled with dilute sulphuric acid, hydrochloric acid, etc., it is converted into aldehyde. The specific gravity of its vapor has been found to be 4.583. This leads to the molecular weight 132.4, and consequently to the formula $C_6H_{12}O_3$. It is called a polymeric modification of aldehyde.

Metaldehyde, $C_6H_{12}O_3$. — Metaldehyde is formed in much the same way as paraldehyde, only a low temperature (below 0°) is most favorable to its formation. It crystallizes in needles, which are insoluble in water, and but slightly soluble in alcohol, chloroform, and ether in the cold, though more readily at a slightly elevated temperature. When heated to 120° in a sealed tube, it is converted into aldehyde. Determinations by the freezing-point method show that the molecular weight of *freshly prepared* metaldehyde is the same as that of paraldehyde. On standing it is converted into paraldehyde and, probably, a substance of the formula $(C_2H_4O)_4$. Distilled with dilute sulphuric acid, etc., metaldehyde is easily converted into aldehyde.

In consequence of the tendency of aldehyde to unite with oxygen, it is a strong reducing agent. When added to an ammoniacal solution of silver nitrate, metallic silver is deposited on the walls of the vessel in the form of a brilliant mirror.

Experiment 15. To a dilute solution of silver nitrate add a solution of ammonia until the silver oxide which is at first precipitated is nearly, though not quite, dissolved; filter, warm gently in a clean test-tube, and add a few drops of a very dilute solution of aldehyde.

A brilliant mirror of metallic silver will appear. This method is used in the manufacture of mirrors. What becomes of the aldehyde?

Chemical transformations of aldehyde. As aldehyde is produced from alcohol by oxidation, so alcohol can be formed from aldehyde by reduction: —

$$C_2H_6O + O = C_2H_4O + H_2O;$$
$$C_2H_4O + H_2 = C_2H_6O.$$

By oxidation aldehyde is converted into an acid of the formula $C_2H_4O_2$, which is acetic acid; and, by reduction, acetic acid is converted into aldehyde: —

$$C_2H_4O + O = C_2H_4O_2;$$
$$C_2H_4O_2 + H_2 = C_2H_4O + H_2O.$$

Treated with phosphorus pentachloride, aldehyde yields *ethylidene chloride*, $C_2H_4Cl_2$ (which see). This reaction is of special interest and importance, as it helps us to understand the relation between aldehyde and alcohol. Alcohol, as has been shown, is the hydroxide of ethyl, $C_2H_5.OH$. When oxidized it loses two atoms of hydrogen. Is the hydrogen of the hydroxyl one of the two which are given off? If so, what readjustment of the oxygen takes place? Such are the questions which we have a right to ask.

To understand the action of phosphorus pentachloride on aldehyde, it will be necessary to consider briefly the action of this reagent in general upon compounds containing oxygen. When it is brought in contact with water, the first change is represented by the equation

$$H_2O + PCl_5 = POCl_3 + 2\ HCl.$$

Next, the oxichloride, $POCl_3$, is acted upon thus: —

$$3\ H_2O + POCl_3 = PO(OH)_3 + 3\ HCl.$$

Or, expressing both changes in one equation, we have: —

$$4\ H_2O + PCl_5 = PO(OH)_3 + 5\ HCl.$$

The phosphorus pentachloride gives up its chlorine and takes up oxygen, or oxygen and hydrogen, in its place. This is the general tendency of the chlorides of phosphorus.

Now, when a chloride of phosphorus is brought together with an alcohol, chlorine is substituted for the oxygen, two atoms of the latter for one of the former, thus: —

$$C_2H_5.OH + PCl_5 = C_2H_5Cl.ClH + POCl_3.$$

But as hydroxyl, $-O-H$, is univalent, its place cannot be taken by two atoms of chlorine and one of hydrogen, and the two chlorine atoms have not the power of linking the hydrogen to the ethyl. Hydrochloric acid is given off, and a compound is formed, which may be regarded as alcohol in which one chlorine atom takes the place of the hydroxyl. This is the kind of action that takes place whenever a chloride of phosphorus acts upon a compound containing hydroxyl; and *hence the reaction is made use of for determining whether hydroxyl is or is not present in a compound.*

When aldehyde is treated with phosphorus pentachloride, the action is entirely different from that just described. Instead of one chlorine atom taking the place of a hydrogen and an oxygen atom, two chlorine atoms take the place of *the oxygen atom*: —

$$C_2H_4O + PCl_5 = C_2H_4Cl_2 + POCl_3.$$

If the explanation above offered of the action of phosphorus pentachloride on alcohol is correct, it follows that aldehyde is not a hydroxyl compound. We can readily understand why two chlorine atoms should take the place of the oxygen atom, if the latter is in combination only with carbon as in carbon monoxide, CO. There is an essential difference between this kind of combination and that which we have in hydroxyl as $C-O-H$. In the latter condition the oxygen serves to connect carbon with hydrogen; in the former it is in combination only with the carbon, and, presumably, the force which holds it can also hold two atoms of chlorine or of any other univalent element with

which it can unite. So that, if oxygen is in a compound in the carbon monoxide condition, we should expect two chlorine atoms to take its place when the compound is treated with phosphorus pentachloride. Let R.CO represent any such compound; then we should have: —

$$RCO + PCl_5 = R.CCl_2 + POCl_3;$$

while, when oxygen is present in the hydroxyl condition, we have: —

$$R.C-O-H + PCl_5 = R.CCl + POCl_3 + HCl.$$

Just as the latter reaction is used to detect the presence of hydroxyl oxygen, so the former is used to detect oxygen in the other condition, which is commonly known as the *carbonyl* condition.

In terms of the valence hypothesis, it is said that in the hydroxyl compounds oxygen is in combination with carbon with one of its affinities, and with hydrogen with the other, while in the carbonyl compounds it is in combination with carbon with both its affinities as represented thus, C= O.

According to the above reasoning aldehyde is a carbonyl compound, or it contains the group CO. The simplest aldehyde must therefore be represented by the formula $H_2C = O$.

Its homologue, acetic aldehyde, is $CH_3.C(=O)-H$. The peculiar properties of aldehyde are believed to be due to the presence of this group, $C(=O)-H$, which is called the aldehyde group. We do not know that the double line in the formula conveys a correct idea in regard to the relation between the carbon and oxygen. All that we know is that these two elements do occur in two different relations to each other, and the formulas C — O — H and C = O recall these relations. They are expressions of facts established by experiment. Our notions in regard to these relations are largely dependent upon the reactions with the chlorides of phosphorus referred to above.

Chloral, trichloraldehyde, $CCl_3.CHO$. — When chlorine acts directly upon aldehyde, complicated reactions take place which need not be discussed here. If, however, water and calcium carbonate are present, substitution takes place, and *trichloraldehyde* is formed. When alcohol is treated with chlorine, a double action takes place: 1st. The alcohol is changed to aldehyde thus: —

$$CH_3.CH_2OH + Cl_2 = CH_3.COH + 2\,HCl.$$

Then the chlorine acts upon the aldehyde, and is substituted for the three hydrogens of the methyl, forming trichloraldehyde: —

$$CH_3.COH + 6\,Cl = CCl_3.COH + 3\,HCl.$$

In reality the aldehyde first formed acts upon the alcohol, forming an intermediate product which is acted upon by the chlorine. The chlorine product thus formed breaks up, forming chloral. The essential features of the reaction, however, are stated in the above equations. Trichloraldehyde is the substance commonly known as chloral. It is simply the tri-chlorine substitution product of aldehyde. It has all the general properties of aldehyde, and the conclusion is therefore justified that it contains the aldehyde group $-\overset{O}{\overset{\|}{C}}H$.

Chloral is a colorless liquid, which boils at 97°, and has the specific gravity 1.54 at 0°.

Note for Student. — Give the formulas of compounds formed when chloral is brought together with ammonia, hydrocyanic acid, and the acid sulphites of the alkalies. What is the formula of the acid formed by its oxidation? The answer is given in the statement that the general chemical conduct of chloral is the same as that of aldehyde.

When chloral and water are brought together, they unite to form a crystallized compound, *chloral hydrate*, $C_2HCl_3O + H_2O$, which is easily soluble in water, and crystallizes from the solution in beautiful, colorless, monoclinic prisms. It melts at 57°

and boils at 97.5°. Taken internally in doses of from 0.6 to 2g, it produces sleep. In larger doses it acts as an anæsthetic.

When treated with an alkali, chloral and chloral hydrate break up, yielding chloroform and formic acid: —

$$\underset{\text{Chloral.}}{CCl_3.COH} + KOH = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Potassium formate.}}{KCHO_2}$$

This reaction, taken together with those which give chloral from alcohol, enables us to understand the reaction which is used in making chloroform and iodoform.

NOTE FOR STUDENT. — How is chloroform made? How is the method explained? Answer the same questions for iodoform. The bleaching powder used in preparing chloroform furnishes chlorine. Is an alkali present?

4. ACIDS.

When methyl and ethyl alcohols are oxidized, they are converted first into aldehydes, and then the aldehydes take up oxygen and are converted into acids. The relations in composition between the hydrocarbons, alcohols, aldehydes, and acids are shown in the subjoined table: —

Hydrocarbons.	Alcohols.	Aldehydes.	Acids.
CH_4	CH_4O	CH_2O	CH_2O_2
C_2H_6	C_2H_6O	C_2H_4O	$C_2H_4O_2$
etc.	etc.	etc.	etc.

The two acids whose formulas are here given are the well-known substances, *formic* and *acetic acids.*

Formic acid, Methanic acid, CH_2O_2. — This acid occurs in nature in red ants, in stinging nettles, in the shoots of some of the varieties of pine, and elsewhere.

It can be prepared by distilling red ants, but is best prepared by heating oxalic acid with glycerol. Oxalic acid has the

composition represented by the formula $C_2H_2O_4$. When heated in glycerol, the effect is to break it up into carbon dioxide and formic acid: —

$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

The formic acid distils over, and can be condensed.

Experiment 16. Into a flask of 500 to 600^{cc} capacity put 200 to 300^{cc} anhydrous glycerol, and then add 30 to 40^{g} crystallized oxalic acid. Connect the flask with a condenser, and insert a thermometer through the cork so that the bulb is below the surface of the glycerol. Heat gently. At 75° to 90°, carbon dioxide is evolved. Raise the temperature gradually to 112°–115°. When formic acid no longer distils over, add another portion of oxalic acid, and heat again. This operation may be repeated a number of times without renewing the glycerol; but, when about 100^{g} of oxalic acid has been decomposed, enough formic acid for the purpose will have been formed, and collected in the receiver. Dilute the distillate to about half a litre, and, while gently warming it in an evaporating dish, add freshly precipitated and washed copper oxide in small quantities until no more is dissolved. Then filter, and evaporate the solution to crystallization. The beautifully crystallized salt thus obtained is copper formate.

The formation of formic acid by oxidation of methyl alcohol, and by treatment of chloral with an alkali, has already been mentioned. The following methods are of special interest: —

(1) By the action of carbon monoxide upon potassium hydroxide: —

$$CO + KOH = H.CO_2K.$$

This method can be used for the preparation of formic acid on the large scale. Soda-lime acts as well as potassium hydroxide.

(2) By the action of metallic potassium upon moist carbon dioxide (carbonic acid): —

$$2\,CO_2 + K_2 + H_2O = HCO_2K + HCO_3K,$$

or

$$2\,CO_3H_2 + K_2 = HCO_2K + HCO_3K + H_2O.$$

(3) By treatment of a solution of ammonium carbonate with sodium amalgam: —

$$CO_3(NH_4)_2 + 2\,H = HCO_2(NH_4) + H_2O + NH_3,$$

and $$HCO_2(NH_4) + NaOH = HCO_2Na + NH_3 + H_2O.$$

According to these last two methods formic acid appears as a reduction product of carbonic acid formed by the abstraction of one atom of oxygen: —

$$H_2CO_3 = H_2CO_2 + O.$$

It is extremely important to bear this fact in mind, as it is of great assistance in enabling us to understand the relation existing between the two acids, and between them and all other acids of carbon. It will be shown that all the acids of carbon may be regarded as derivatives of either formic acid or carbonic acid.

(4) When hydrocyanic acid is treated with an acid or an alkali, it breaks up, forming ammonia and formic acid. The reaction may be represented thus: —

$$HCN + 2\,H_2O = H_2CO_2 + NH_3.$$

Of course, if an acid is present, the ammonium salt of the acid is formed; and, if an alkali is present, the formate of this alkali is formed. *A reaction similar to this is used very extensively in the preparation of the acids of the carbon*, as will be shown.

Anhydrous formic acid can be made by dehydrating either the copper or lead salt, and passing dry hydrogen sulphide over the salt placed in a heated tube. The acid distils over, and can be obtained perfectly pure by placing a little of the anhydrous salt in it and redistilling

It is a colorless liquid which boils at 100.6° at 760^{mm}. It has a penetrating odor. Dropped on the skin, it causes extreme pain and produces blisters. Its specific gravity at 0° is 1.22. When cooled down it solidifies to a mass of crystals which melt at 8.6°.

Concentrated sulphuric acid decomposes it into carbon monoxide and water : —

$$H_2CO_2 = CO + H_2O.$$

It is easily oxidized to carbonic acid. Hence it acts as a reducing agent. Heated with the oxides of mercury or silver, they are reduced to the metallic condition : —

$$HgO + H_2CO_2 = Hg + H_2O + CO_2.$$

Like other acids, formic acid yields a large number of salts with bases, and ethereal salts or compound ethers with the alcohols. These derivatives may not be treated of here. The salts are all soluble in water, and some of them, as the lead, copper, and barium salts, crystallize very well. Some of the compound ethers will be mentioned when these substances are considered as a class.

Acetic acid, Ethanic acid, $C_2H_4O_2$. — The two methods by which acetic acid is exclusively made are, —

(1) By the oxidation of alcohol ; and

(2) By the distillation of wood.

When pure alcohol is exposed to the air it undergoes no change. If, however, some platinum black is placed in it, oxidation takes place and acetic acid is formed. So also if fermented liquors which contain nitrogenous substances are exposed to the air, oxidation takes place, and the liquor becomes sour in consequence of the formation of acetic acid. A great deal of acetic acid is made by exposing poor wine to the action of the air. The product is known as *wine vinegar*. The formation of vinegar has been shown to be due to the presence of a microscopic organism (*Mycoderma aceti*) commonly known as "mother-of-vinegar." This serves in some way to convey the oxygen from the air to the alcohol. The "quick-vinegar process," much used in the manufacture of vinegar, consists in allowing weak spirits of wine to pass slowly through barrels

filled with beech shavings which have become covered with *Mycoderma aceti*. The presence of the organism is secured by first pouring strong vinegar into the barrels, and allowing it to stand for one or two days in contact with the shavings.

When wood is distilled, a very complex mixture passes over, one of the constituents being acetic acid. By keeping the temperature down comparatively low, the amount of acetic acid obtained is increased. The distillate is neutralized with soda ash, and the solution of crude sodium acetate thus obtained evaporated to dryness. It is then treated with sulphuric acid, and distilled, when acetic acid passes over.

Besides the two methods mentioned, there are two others which may be used for making acetic acid. One of them is a modification of a method referred to under formic acid, and, from the scientific point of view, both are of great interest. They are,—

(1) By treating carbon dioxide with a compound known as *sodium-methyl*, which may be regarded as marsh gas, in which one hydrogen is replaced by sodium as shown in the formula CH_3Na:—

$$CO_2 + CH_3Na = CH_3.CO_2Na.$$

(2) By treating methyl cyanide, CH_3CN, with an acid or an alkali:—

$$CH_3CN + 2\,H_2O = CH_3.CO_2H + NH_3.$$

This reaction is analogous to that involved in the formation of formic acid from hydrocyanic acid (see p. 56).

Whether the acid is made from alcohol or from wood, it must be purified. For this purpose it is passed through charcoal and distilled. It still contains water, from which it cannot be completely separated by distillation. When cooled down to a sufficiently low temperature it solidifies, and the water can then partly be poured off. By repeating the freezing, and distilling a few times, perfectly pure, anhydrous acetic acid can be obtained.

Experiment 17. Make pure acetic acid from the commercial substance. First distil in fractions until a portion is obtained that boils between 110° and 119°. Put the vessel containing this in ice. The liquid will solidify almost completely. Pour off the little liquid which remains, and distil.

Acetic acid is a clear, colorless liquid, which boils at 118°. It has a very penetrating, pleasant, acid odor, and a sharp acid taste. *The pure substance acts upon the skin like formic acid, causing pain and raising blisters.* It solidifies when cooled down, and the crystals melt at 16.7°. The pure acid which is solid at temperatures below 16° is known as *glacial acetic acid.* Its specific gravity is 1.08 at 0°. It mixes with water in all proportions.

Acetic acid is extensively used, chiefly in the dilute, impure form known as vinegar. Formic acid would answer perhaps as well. It is used in calico printing in the form of iron and aluminium salts. With iron it gives hydrogen, which is needed in the manufacture of certain compounds used in making dyes, as, for example, aniline. It is an excellent solvent for many organic substances, and is therefore frequently used in scientific researches.

Derivatives of acetic acid. Acetic acid yields a very large number of derivatives. They may be considered briefly under two heads: (1) Those which are formed in consequence of the acid properties and which necessitate a loss of the acid properties, as the salts, ethereal salts, etc.; and (2) those in which the acid properties remain essentially unchanged.

Salts of acetic acid. The acetates of the alkalies were the first compounds of carbon ever prepared. The *potassium* and *sodium* salts are used in the chemical laboratory. Both crystallize, the sodium salt particularly well and easily.

Lead acetate, $(C_2H_3O_2)_2Pb$. This salt, which is commonly known as *sugar of lead*, is made on the large scale by dissolving lead oxide in acetic acid. It crystallizes well, and is soluble in 1.5 parts of water at ordinary temperatures. Commercial sugar of lead frequently contains an excess of lead oxide in

the form of basic salts. A solution of such a mixture becomes turbid when allowed to stand in the air, or gives a precipitate when dissolved in ordinary spring water, in consequence of the formation of lead carbonate.

Copper acetate, $(C_2H_3O_2)_2Cu$. This salt can be made by dissolving copper hydroxide or carbonate in acetic acid. It crystallizes in dark-blue, transparent prisms. A *basic acetate*, formed by the action of acetic acid on copper in the air, is known as *verdigris*.

Copper aceto-arsenite, $3\,CuAs_2O_4 + (C_2H_3O_2)_2Cu$. This double salt is formed by boiling verdigris and arsenic trioxide together in water. It has a fine bright-green color, and is used as a pigment and as an insecticide. It is the chief constituent of emerald green, Paris green, or Schweinfurt's green.

Iron forms two distinct salts with acetic acid, the *ferrous* salt, $(C_2H_3O_2)_2Fe + 4\,H_2O$, and the *ferric* salt, $(C_2H_3O_2)_6Fe_2$. The latter is formed when sodium acetate is added to an acidified solution of a ferric salt. At first the solution becomes deep-red in color; but, on boiling, all the iron is precipitated as hydroxide. Hence this salt is used for the purpose of separating iron from manganese in analytical operations.

Experiment 18. To a dilute solution of ferric chloride, contained in a small flask, add a little acetic acid and a solution of sodium acetate. Boil the red solution, and ferric hydroxide is precipitated, leaving the solution colorless. Filter, and examine the filtrate for iron.

The ethereal salts will be mentioned briefly when this class of compounds is considered. The principal one is *ethyl acetate* or *acetic ether*, which is formed from acetic acid and ordinary alcohol. When a mixture of these two substances is treated with sulphuric acid, the ether is formed and can be recognized by its pleasant odor. This fact is taken advantage of for the detection of acetic acid.

Experiment 19. To a mixture of about equal parts of acetic acid and alcohol, in a test-tube, add a little concentrated sulphuric acid, heat, and notice the odor. It is that of ethyl acetate or acetic ether.

Acetic anhydride or acetyl oxide, $C_4H_6O_3$. — This substance, which bears to acetic acid the relation of an anhydride, is made by abstracting water from the acid: —

$$2\,C_2H_4O_2 = C_4H_6O_3 + H_2O.$$

Like other acids, acetic acid contains hydroxyl, as will be shown below. We may hence represent the acid thus: $C_2H_3O.OH$. The part C_2H_3O is known as acetyl. Now when water is abstracted from the acid, the change takes place as represented in this equation: —

$$\left.\begin{matrix} C_2H_3O.OH \\ C_2H_3O.OH \end{matrix}\right\} = \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + H_2O.$$

Hence, according to this, acetic anhydride appears as the oxide of acetyl, while the acid itself is the hydroxide.

Acetic anhydride is a colorless liquid which boils at 138°. With water it gives acetic acid.

Acetyl chloride, C_2H_3OCl.
Acetyl bromide, C_2H_3OBr.
Acetyl iodide, C_2H_3OI.

Just as alcohol, when treated with phosphorus trichloride, yields a chloride of ethyl, so acetic acid, when treated with the same reagent, yields acetyl chloride. The character of the reaction is the same in both cases. It consists in the replacement of hydroxyl by chlorine: —

$$3\,C_2H_3O.OH + PCl_3 = 3\,\underset{\text{Acetyl chloride.}}{C_2H_3OCl} + P(OH)_3.$$

Experiment 20. Arrange a *dry* distilling flask, with condenser and *dry* receiver, under a hood or out of doors. Bring together 9 parts (say 180ᵍ) strong acetic acid and 6 parts (say 120ᵍ) phosphorus trichloride. Slightly heat the mixture on the water-bath, when acetyl chloride will distil over. Collect in a dry bottle.

Acetyl chloride is a colorless liquid which boils at 55°. Water acts upon it very readily, acetic and hydrochloric acids being formed: —

$$C_2H_3OCl + H_2O = C_2H_3O.OH + HCl.$$

In this case the chlorine is replaced by hydroxyl. As the substance is volatile, it fumes in contact with the air in consequence of the formation of hydrochloric acid. It must be kept in tightly-stoppered bottles. In handling it, care must be taken not to bring it near the nose, as its odor is very suffocating, and it attacks the mucous membranes of the eyes and nose, producing coughing and other bad results.

Acetyl chloride is a valuable reagent much used in the examination of compounds of carbon. Its value depends upon its action towards alcohols. When it is brought together with an alcohol, as, for example, methyl alcohol, hydrochloric acid is evolved, and the acetyl group takes the place of the hydrogen of the alcoholic hydroxyl: —

$$CH_3.OH + C_2H_3OCl = CH_3.O.C_2H_3O + HCl.$$

The product is an ethereal salt, methyl acetate. This kind of action takes place whenever an alcohol is treated with acetyl chloride. Hence if, on treating a substance with acetyl chloride, its composition is changed, showing that hydrogen is replaced by acetyl, we are justified in concluding that the substance contains alcoholic hydroxyl. The bromide and iodide resemble the chloride very closely.

Experiment 21. Treat a few cubic centimetres of *absolute* alcohol with acetyl chloride. Notice the evolution of hydrochloric acid and the odor of ethyl acetate.

Substitution-products of acetic acid. These bear the same relation to acetic acid that the substitution-products of marsh gas bear to marsh gas. They are formed by the simple substitution of a halogen, etc., for hydrogen. Only three of the four hydrogen atoms of acetic acid are capable of direct replacement. The fourth is the one to which the acid properties are due. Hence the substitution-products are acid. The best known of these products are the chlor-acetic acids which are made by treating the acid with chlorine. They are

mono-chlor-acetic, *di-chlor-acetic*, and *tri-chlor-acetic acids.* Their formation is represented by the following equations: —

$$C_2H_3O.OH + Cl_2 = C_2H_2ClO.OH + HCl;$$
$$C_2H_2ClO.OH + Cl_2 = C_2HCl_2O.OH + HCl;$$
$$C_2HCl_2O.OH + Cl_2 = C_2Cl_3O.OH + HCl.$$

When treated with nascent hydrogen they are converted back into acetic acid. They yield salts, ethereal salts, anhydrides, etc., just the same as acetic acid itself.

Theory in regard to the relations between the acids, alcohols, aldehydes, and hydrocarbons. The reactions and methods of formation of acetic acid enable us to form a clear conception in regard to the relation of its constituents. In the first place the presence of hydroxyl is shown by the reaction with phosphorus trichloride. We hence have $C_2H_3O.OH$ as the formula representing this idea. But several questions still remain to be answered. There is another oxygen atom to be accounted for; and the relations between the hydroxyl and this oxygen must be determined if possible. The fact that this second oxygen is not readily replaced by chlorine indicates that it is not present as hydroxyl, and all methods of testing for hydroxyl fail to show its presence in acetyl chloride. Hence we may conclude that the second oxygen atom is present as carbonyl CO. This leads us to the formula $H-C(=O)-O-H$ for the simplest acid, or formic acid. Accordingly, formic acid appears as carbonic acid, which is commonly represented by the formula $O=C(OH)(OH)$, in which one hydroxyl has been reduced to hydrogen. We have already seen that this reduction can be accomplished without difficulty. Many other arguments might be brought forward in favor of the view that the above formulas express the relations between formic and carbonic acids. Now, as acetic acid is the homologue of formic acid, we have every

reason to believe that it differs from the latter in that it contains methyl in place of the hydrogen, which is in direct combination with carbon, and this view is confirmed by the fact that acetic acid can be made from sodium methyl, CH_3Na, and from methyl cyanide, $CH_3.CN$. The acid must hence be represented by the formula $CH_3.\overset{\overset{O}{\|}}{C}-OH$ or $CO<\begin{matrix}CH_3\\OH\end{matrix}$. The common constituent of the two acids is the group $\overset{\overset{O}{\|}}{C}-O-H$ or $-CO.OH$, which is generally known as *carboxyl*. Acetic acid is closely related not only to formic but to carbonic acid. It may be regarded as carbonic acid, $CO<\begin{matrix}OH\\OH\end{matrix}$, in which one hydroxyl is replaced by the radical methyl. In a similar way we shall see that all organic acids may be regarded as derived either from formic acid or from carbonic acid. Representing now the simplest hydrocarbon, alcohol, aldehyde, and acid, by the structural formulas deduced from the facts, we have

$C\begin{cases}H\\H\\H\\H\end{cases}$	$C\begin{cases}OH\\H\\H\\H\end{cases}$	$C\begin{cases}O\\H\\H\end{cases}$	$C\begin{cases}O\\OH.\\H\end{cases}$
Marsh gas (Methane).	Methyl alcohol (Methanol).	Formic aldehyde (Methanal).	Formic acid (Methanic acid).

Concerning the mechanism of the changes caused by oxidation, but little can be determined by experiment. We may regard methyl alcohol as the first and simplest product of oxidation of marsh gas. Starting with methyl alcohol, we might expect the next change to consist in the introduction of another oxygen atom, giving a body $C\begin{cases}OH\\OH.\\H\\H\end{cases}$. But it has been found that, except under certain peculiar conditions, one carbon atom cannot hold two hydroxyls in combination, and

that, if such a compound is formed, it loses the elements of water, thus, $C\begin{cases} OH \\ OH \\ H \\ H \end{cases} = C\begin{cases} O \\ H \\ H \end{cases} + H_2O$. The result would be the aldehyde. This kind of change is illustrated in the formation of carbon dioxide from the salts of carbonic acid. Instead of getting the acid $CO<\begin{matrix} OH \\ OH \end{matrix}$, which we should naturally expect, we get this minus water: —

$$CO<\begin{matrix} OH \\ OH \end{matrix} = CO_2 + H_2O.$$

Now, when the aldehyde is oxidized, another oxygen atom is introduced, and the substance thus produced is an acid, or the hydroxyl hydrogen can be replaced by metals, and has in general the characteristics of acid hydrogen. As soon as we have carbon in combination with oxygen as carbonyl, and also with hydroxyl, the substance containing the combination is an acid.

If, finally, the acid $C\begin{cases} O \\ OH \\ H \end{cases}$ is oxidized, it is probable that the same change takes place as when the alcohol is oxidized. That is to say, the hydrogen is probably replaced by hydroxyl, when a compound containing two hydroxyls in combination with one carbon atom would be the result. This would be ordinary carbonic acid. But this breaks up into water and carbon dioxide, which, as we know, are the products of oxidation of formic acid.

All the many representatives of the great classes of carbon compounds known as the alcohols, aldehydes, and acids are closely related to the three fundamental substances, methyl alcohol, formic aldehyde, and formic acid. Replace one of the hydrogen atoms of methyl alcohol by a radical, and we get a new alcohol, which may be represented by the formula $C\begin{cases} OH \\ H \\ H \\ R \end{cases}$. So also a similar replacement of a hydrogen atom in formic

aldehyde gives another aldehyde, $C\begin{cases} O \\ H \\ R \end{cases}$; and, finally, as we have seen, the acids of carbon may be represented by the formulas $C\begin{cases} O \\ OH \\ R \end{cases}$, or R.CO.OH, or $CO<\begin{matrix} R \\ OH \end{matrix}$, which show their relations to formic and carbonic acids. Hereafter, in writing the formulas of members of the three great classes, the structure will be represented by writing the hydroxyl group OH, the aldehyde group CHO, and the carboxyl group CO.OH or CO_2H, separately from the rest of the formula.

5. Ethereal Salts or Esters.

Whenever an acid acts upon an alcohol, the acid is neutralized either wholly or partly, and a product analogous to the salts is formed. Thus nitric acid and ethyl alcohol give ethyl nitrate: —

$$C_2H_5.OH + HNO_3 = C_2H_5.NO_3 + H_2O,$$

just as nitric acid and potassium hydroxide give potassium nitrate. It has been pointed out that the radicals, methyl, CH_3, and ethyl, C_2H_5, take the part of metals in the ethereal salts. We can thus get a series of methyl and ethyl salts with the various acids.

As regards the preparation of these compounds, it should be remarked that the action between an alcohol and an acid does not take place as readily as that between an acid and a metallic hydroxide. Only a few of the strongest acids act directly without aid. Such, for example, are nitric and sulphuric acids, though even the latter is not completely neutralized by action upon alcohols, as has already been seen in the preparation of ethyl-sulphuric acid, $\begin{matrix} C_2H_5 \\ H \end{matrix}>SO_4$, for the purpose of making ether. Plainly ethyl-sulphuric acid is an acid ethereal salt, analogous to acid potassium sulphate. Both are still acid, though both are likewise salts.

The methods which may be used for preparing ethereal salts are the following: —

(1) Treatment of an acid with an alcohol. This is capable of only very limited application, as in the case of a few of the strongest acids.

(2) Treatment of the chloride of an acid with alcohol. This has been illustrated by the action of acetyl chloride, $C_2H_3O.Cl$, upon methyl alcohol (see p. 62): —

$$C_2H_3OCl + HO.CH_3 = C_2H_3O.OCH_3 + HCl,$$

or $$CH_3.COCl + HO.CH_3 = CH_3.COOCH_3 + HCl.$$

(3) Treatment of the silver salt of an acid with a halogen substitution-product of a hydrocarbon. For example, ethyl acetate can be made by treating silver acetate with bromethane: —

$$CH_3.COOAg + C_2H_5Br = CH_3COOC_2H_5 + AgBr.$$

This reaction is well adapted to showing the relation between the salt and the ethereal salt, and leaves no room for doubt that the two are strictly analogous.

(4) Treatment of a mixture of an alcohol and an acid with dry hydrochloric acid gas or strong sulphuric acid. The formation of ethyl acetate by this method was illustrated in Experiment 19, p. 60. The sulphuric acid facilitates the action by uniting with the alcohol to form ethyl-sulphuric acid, which with the acid gives the ethereal salt: —

$$\begin{matrix} C_2H_5 \\ H \end{matrix} > SO_4 + CH_3.COOH = CH_3.COOC_2H_5 + H_2SO_4.$$

It is probable that the hydrochloric acid first acts upon the acid forming the chloride, and that this then acts upon the alcohol, forming the ethereal salt: —

$$CH_3.COOH + HCl = CH_3.COCl + H_2O;$$
$$CH_3.COCl + C_2H_5OH = CH_3.COOC_2H_5 + HCl.$$

Among the more important ethereal salts of methyl and ethyl alcohols, the following may be mentioned: —

Methyl-sulphuric acid, $\begin{matrix}CH_3\\H\end{matrix}\!>\!SO_4$, formed by mixing methyl alcohol and sulphuric acid. The acid itself, as well as its salts, is very easily soluble in water.

Ethyl nitrate, $C_2H_5NO_3$, formed by treating alcohol with nitric acid. Unless precautions are taken in mixing these reagents, complete decomposition of the alcohol will take place, and the action will be accompanied by a violent explosion.

Ethyl-sulphuric acid, $\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_4$. Made in the same way as the methyl compound. The acid and its salts are easily soluble in water. When boiled with water it is decomposed, yielding alcohol and sulphuric acid: —

$$\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_4 + H_2O = H_2SO_4 + C_2H_5OH.$$

Ethyl sulphate, $(C_2H_5)_2SO_4$, is made by passing the vapor of sulphur trioxide into well-cooled ether: —

$$(C_2H_5)_2O + SO_3 = (C_2H_5)_2SO_4.$$

Phosphoric acid yields *ethyl phosphate*, $(C_2H_5)_3PO_4$, *di-ethyl-phosphoric acid*, $(C_2H_5)_2HPO_4$, and *ethyl-phosphoric acid*, $C_2H_5H_2PO_4$.

There also are similar derivatives of arsenic, boric, silicic, and other mineral acids.

Of the ethereal salts which the two alcohols form with formic and acetic acids, *methyl* and *ethyl acetates* are the best known. The methods of preparing them have already been given. They are both liquids having pleasant odors. This is indeed a characteristic of many of the volatile ethereal salts of the acids of carbon, and many of the odors of fruits and flowers are due to the presence of one or another of these compounds. Many

of them also are used for flavoring purposes instead of the natural substances.

Experiment 22. Make a mixture of 15 parts (150g) of ordinary concentrated sulphuric acid and 6 parts (60g) absolute alcohol. Add to it 10 parts (100g) sodium acetate. Distil from a flask. Redistil the distillate. The ethyl acetate thus formed boils at 77°. What reactions take place in this case?

Decomposition of ethereal salts. Salts of most metals are decomposed when treated with an alkaline hydroxide, as caustic soda or caustic potash, the result being a salt of the alkali and the hydroxide of the replaced metal, as seen in the case of copper sulphate and sodium hydroxide: —

$$CuSO_4 + 2\,NaOH = Cu(OH)_2 + Na_2SO_4.$$

So also the ethereal salts are decomposed when treated with the alkalies, though, as a rule, not as readily as salts. It is usually necessary to boil the ethereal salt with the alkali when decomposition takes place, the radical, like the metal, appearing in the form of the hydroxide or alcohol, and the alkali metal taking its place. Thus, when ethyl sulphate is treated with a solution of caustic potash, this reaction takes place: —

$$(C_2H_5)_2SO_4 + 2\,KOH = K_2SO_4 + 2\,C_2H_5.OH;$$

and when ethyl acetate is treated with caustic soda, we have this reaction: —

$$CH_3.COOC_2H_5 + NaOH = CH_3.COONa + C_2H_5OH.$$

Experiment 23. In a 500cc flask put 200cc water, 50g solid caustic potash, and 20cc ethyl acetate. Connect with an inverted condenser, arranged as shown in Fig. 8. Boil gently for half an hour. Now connect the condenser with the flask for distilling, and again boil. Examine the distillate for alcohol. Acidify the contents of the flask with sulphuric acid, and again distil. What passes over?

All ethereal salts are decomposed by boiling with the caustic alkalies. As this decomposition is best known on the large scale in the preparation of soaps, it is commonly called *saponification*.

As will be shown, the fats are ethereal salts, and soap-making consists in decomposing these fats by means of the alkalies. Hence, generally, to *saponify* an ethereal salt means to decompose it by means of an alkali into the corresponding alcohol and the alkali salt of the acid contained in it.

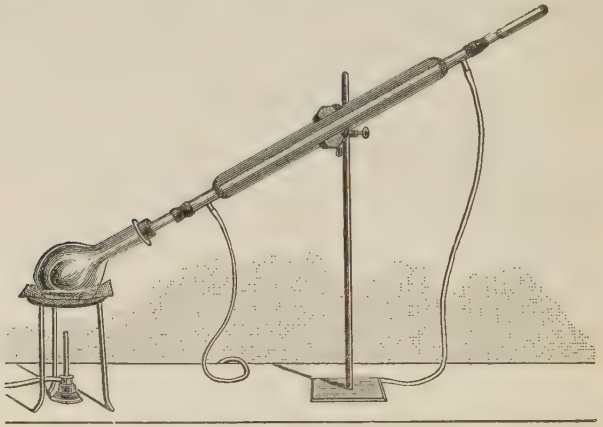


Fig. 8.

6. Ketones or Acetones.

When an acetate is distilled, a liquid passes over which has the composition C_3H_6O, and a carbonate remains behind. The reaction has been carefully studied, and has been shown to take place in accordance with the following equation: —

$$\left.\begin{matrix}CH_3.COO\\CH_3.COO\end{matrix}\right\rangle Ca = C_3H_6O + CaCO_3.$$

The substance C_3H_6O is known as *acetone*. It is the best known representative of a class of compounds which are sometimes called *acetones*, but more commonly *ketones*.

Acetone, Dimethylketone, Propanone, C_3H_6O. — This substance has long been known as a product of the distillation of acetates. It is contained in considerable quantities in the

product obtained in the distillation of wood, and can be separated from the mixture after the removal of the acetic acid.

It can be purified by shaking a mixture containing it with a concentrated solution of mono-sodium sulphite. It unites with the salt, forming a compound analogous to that formed with aldehyde. The double compound can be separated, and when distilled with the addition of potassium carbonate acetone passes over.

Acetone is a colorless liquid having a penetrating pleasant ethereal odor. It boils at 56.3°. It is a good solvent for many carbon compounds, such as resins, fats, etc.

On studying the conduct of acetone, it soon becomes evident that it more closely resembles the aldehydes than any other bodies thus far considered. It is plainly not an acid nor an alcohol. It acts entirely differently from either. It is not an ethereal salt, for on boiling with an alkali it does not yield an alcohol nor the salt of an acid. On the other hand, it unites with the acid sulphites like the aldehydes. Further, when treated with phosphorus pentachloride its oxygen is replaced by two chlorine atoms thus: —

$$C_3H_6O + PCl_5 = C_3H_6Cl_2 + POCl_3;$$

and when treated with nascent hydrogen, it is converted into a substance having alcoholic properties. These facts lead to the conclusion that the substance contains carbonyl, CO, as the aldehydes do. This is shown in the formula C_2H_6CO. The formation from calcium acetate leads further to the belief that the group C_2H_6 really consists of two methyls, as the simplest interpretation of the reaction is represented thus: —

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} > Ca = \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CO + CaCO_3.$$

According to this, acetone is a compound of two methyl groups and carbonyl, or it is carbon monoxide whose two available affinities have been satisfied by two methyl groups.

We can test the correctness of this view by means of syntheses. If it is correct, it will be seen that acetone is closely related to acetyl chloride. It is acetyl chloride in which the chlorine has been replaced by methyl: —

$CH_3.CO.Cl$ — Acetyl chloride. $CH_3.CO.CH_3$. — Acetone.

Now, when acetyl chloride is treated with zinc methyl, $Zn(CH_3)_2$, it yields acetone according to this equation: —

$$2\,CH_3.COCl + Zn(CH_3)_2 = 2\,CH_3.CO.CH_3 + ZnCl_2.$$

The relation between acetone and ordinary acetic aldehyde is similar to that of an ethereal salt to its acid; that is, acetone is aldehyde, $CH_3.COH$, in which the hydrogen has been replaced by methyl, $CH_3.CO.CH_3$.

Like the aldehydes, the acetone has the power of taking up other substances, such as the acid sulphites, ammonia, hydrocyanic acid, hydrogen, etc. This power is in some way connected with the relation of the oxygen to the carbon, which is the same in both compounds. Nevertheless, this condition of the oxygen does not always carry with it the same power as seen in the case of the acids which also contain carbonyl.

By reduction with nascent hydrogen, acetone yields an alcohol of the formula C_3H_8O, known as *secondary propyl alcohol*, which when oxidized yields acetone. In other words, the relation between this alcohol and acetone is much the same as that between ethyl alcohol and acetic aldehyde. But while the aldehyde by further oxidation yields acetic acid by simply taking up one atom of oxygen, acetone is decomposed by oxidizing agents, and yields acetic and carbonic acids. Towards oxidizing agents, then, acetones (for it will be shown that other acetones conduct themselves in the same way) act entirely differently from the aldehydes. The alcohol above mentioned

as related to acetone is the simplest representative of a class of alcohols differing in some respects from the substances commonly called alcohols.

We have thus considered the most important representatives of six classes of oxygen derivatives of the hydrocarbons, and, by a study of their chemical conduct and the methods available for their preparation, have formed views in regard to the relations between them. In our ordinary language we may express these relations briefly thus: The alcohols are the hydroxyl derivatives of the hydrocarbons or the hydroxides of certain groups called *radicals;* the ethers are the oxides of these same radicals; the aldehydes are compounds consisting of carbonyl, hydrogen, and a radical; the acids are compounds of carbonyl, hydroxyl, and a radical, or, better, they are carbonic acid in which hydrogen and oxygen, or hydroxyl, have been replaced by a radical; the ethereal salts are compounds like ordinary metallic salts, only they contain a radical in the place of the metal; and, finally, the ketones are aldehydes in which the distinctively aldehyde hydrogen has been replaced by a radical, or they are compounds consisting of carbonyl and two radicals.

These ideas are expressed in formulas thus, R being any univalent radical like methyl, CH_3, or ethyl, C_2H_5: —

Alcohol . . . . R—O—H.

Ether . . . . . R—O—R.

Aldehyde . . . . R—C—H.
‖
O

Acid . . . . . R—C—O—H.
‖
O

Ethereal salt . . Ac—O—R (Ac—O—H representing any monobasic acid).

Ketone . . . . R—C—R.
‖
O

CHAPTER V.

SULPHUR DERIVATIVES OF METHANE AND ETHANE.

1. Mercaptans.

The simplest derivatives of methane and ethane containing sulphur are the so-called *mercaptans* or *sulphur alcohols*. They can be made by a method similar to one described under the head of Alcohols. When a mono-halogen derivative of a hydrocarbon, as brom-methane, CH_3Br, is treated with the hydroxide of a metal, as silver hydroxide, AgOH, an alcohol is formed: —

$$CH_3Br + AgOH = CH_3OH + AgBr.$$

So, also, when a similar halogen derivative is treated with a *hydrosulphide* instead of a *hydroxide*, a compound is obtained which may be regarded as an alcohol in which the oxygen has been replaced by sulphur: —

$$CH_3Br + KSH = CH_3SH + KBr.$$

The compound is called a *mercaptan*.

Ethyl-mercaptan, $C_2H_5.SH$. — This substance can be prepared by treating iodo-ethane, C_2H_5I, with an alcoholic solution of potassium hydrosulphide, KSH; also by distilling a mixture of the concentrated solutions of potassium ethylsulphate and potassium hydrosulphide: —

$$\begin{matrix} C_2H_5 \\ K \end{matrix} > SO_4 + KSH = K_2SO_4 + C_2H_5SH.$$

It is a liquid of an *extremely disagreeable odor;* it boils at 37°; and is difficultly soluble in water.

The name "mercaptan" was given to it on account of its action towards mercury. It readily forms a compound in which mercury takes the place of hydrogen, $(C_2H_5S)_2Hg$; and the name has reference to this power (*mercurium captans*). It

forms many other well-characterized metallic derivatives like this mercury compound.

When the sodium compound of mercaptan is exposed to the air, it takes up oxygen. So, also, when mercaptan itself is treated with nitric acid, it is oxidized, the product having the formula $C_2H_5.SO_3H$. It will thus be seen that, though in composition mercaptan is analogous to alcohol, towards oxidizing agents it conducts itself quite differently. In the case of alcohol two atoms of hydrogen are replaced by one of oxygen. In the case of mercaptan three atoms of oxygen are added directly to the molecule. It will be shown that this new acid, which is called *ethyl-sulphonic acid*, bears to sulphuric acid a relation similar to that which acetic acid bears to carbonic acid; and that it bears to sulphurous acid a relation similar to that which acetic acid bears to formic acid.

When treated with phosphorus pentachloride it yields a chloride, $C_2H_5.SO_2Cl$; and, when this is treated with nascent hydrogen (zinc and hydrochloric acid), it is reduced to mercaptan: —

$$C_2H_5.SO_2Cl + 6\,H = C_2H_5.SH + HCl + 2\,H_2O.$$

2. Sulphur Ethers.

There are compounds known similar to the ethers, containing sulphur in the place of the oxygen of the ethers. Such are methyl sulphide, $(CH_3)_2S$, and ethyl sulphide, $(C_2H_5)_2S$. These are made by treating brom- or iodo-methane or ethane with potassium sulphide: —

$$2\,C_2H_5I + K_2S = (C_2H_5)_2S + 2\,KI;$$

or by treating the sodium salt of methyl or ethyl-mercaptan with methyl or ethyl iodide: —

$$C_2H_5.SNa + C_2H_5I = (C_2H_5)_2S + NaI.$$

They are liquids with very disagreeable odors. When oxidized they are converted into sulphones, two atoms of oxygen being added, thus $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!S + O_2 = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!SO_2$.

3. Sulphonic Acids.

It was stated above, that when mercaptan is oxidized it is converted into an acid of the formula $C_2H_5 . SO_3H$, or *ethyl-sulphonic acid.* This is the representative of a large class of substances which are commonly made by treating carbon compounds with sulphuric acid. These sulphonic acids can best be studied in connection with another series of hydrocarbons. Under the head of Benzene (which see) it will be shown that, when this hydrocarbon is treated with sulphuric acid, a reaction takes place which may be represented thus: —

$$\underset{\text{Benzene.}}{C_6H_6} + \begin{matrix}HO\\HO\end{matrix}\!>\!SO_2 = \underset{\text{Benzene-sulphonic acid.}}{\begin{matrix}C_6H_5\\HO\end{matrix}\!>\!SO_2} + H_2O.$$

The sulphonic acid thus obtained can also be made by oxidizing the corresponding mercaptan or hydrosulphide, $C_6H_5 . SH$. Accordingly, the sulphonic acid appears to be sulphuric acid in which a hydroxyl has been replaced by the radical C_6H_5. Reasoning by analogy, which, fortunately, is supported by other arguments, we may conclude that ethyl-sulphonic acid formed from ethyl-mercaptan bears a similar relation to sulphuric acid, and corresponds to the formula $\begin{matrix}C_2H_5\\HO\end{matrix}\!>\!SO_2$. So, also, methyl-sulphonic acid obtained by oxidation of methyl-mercaptan should be represented by the formula $\begin{matrix}CH_3\\HO\end{matrix}\!>\!SO_2$ or $CH_3 . SO_2OH$. *Its relation to sulphuric acid is the same as that of acetic acid to carbonic acid.*

Another method by which the sulphonic acids can be prepared consists in treating a sulphite with a halogen substitution-product. Thus ethyl-sulphonic acid can be prepared from potassium sulphite and iodo-ethane: —

$$C_2H_5I + \begin{matrix}K\\K\end{matrix}\!>\!SO_3 = \begin{matrix}C_2H_5\\K\end{matrix}\!>\!SO_3 + KI,$$

or

$$C_2H_5I + \begin{matrix}K\\KO\end{matrix}\!>\!SO_2 = \begin{matrix}C_2H_5\\KO\end{matrix}\!>\!SO_2 + KI.$$

According to this reaction the sulphonic acids appear to be identical with the ethereal salts of sulphurous acid, but they do not conduct themselves like ethereal salts. The difference is particularly noticeable in connection with the stability, the sulphonic acids as a class being much more stable than the ethereal salts as a class. At present it would be somewhat premature to discuss fully the question as to their relations. Whatever we may call them, they are closely related to sulphurous acid, and are derived from it by replacement of hydrogen by a radical, just as acetic acid may be regarded as derived from formic acid by replacement of hydrogen by a radical. These relations are represented by the following formulas: —

Carbonic acid,	$CO<\frac{OH}{OH}$.	Sulphuric acid,	$SO_2<\frac{OH}{OH}$.
Formic acid,	$CO<\frac{H}{OH}$.	Sulphurous acid,	$SO_2<\frac{H}{OH}$.
Acetic acid,	$CO<\frac{CH_3}{OH}$.	Methyl-sulphonic acid,	$SO_2<\frac{CH_3}{OH}$.
Any carbonic acid,	$CO<\frac{R}{OH}$.	Any sulphonic acid,	$SO_2<\frac{R}{OH}$.

The difference between a sulphonic acid and an ethereal salt of sulphuric acid should be specially noticed. Compare for this purpose ethyl-sulphuric acid, $\frac{C_2H_5O}{HO}>SO_2$, and ethyl-sulphonic acid, $\frac{C_2H_5}{HO}>SO_2$. Both are monobasic acids, and both contain ethyl, but there is a difference of one atom of oxygen in their composition. The reactions of the substances are such as to lead to the conclusion that in ethyl-sulphonic acid the ethyl group is directly connected with the sulphur; and that in ethyl-sulphuric acid the connection is established by means of oxygen. The strongest argument in favor of this view is perhaps that which is founded on the formation of the sulphonic acids by oxidation of the hydrosulphides or mercaptans. It

can hardly be doubted that in ethyl-mercaptan the sulphur is in direct combination with the ethyl; or, to go still farther, that it is in combination with carbon as represented in the formula $H_3C-\overset{H}{\underset{H}{C}}-S-H$. Now, by oxidation of mercaptan, three atoms of oxygen are added, and the simplest view we can take of the reaction is that the sulphur is left undisturbed in its relations to ethyl, but that it has taken up the oxygen, as represented in the formula $C_2H_5-SO_2.OH$. As has been shown, the oxygen can be removed again by nascent hydrogen, and the result is mercaptan. The study of the sulphonic acids in their relations to sulphuric and sulphurous acids has been of considerable assistance in enabling chemists to form conceptions in regard to the relations of the constituents of the two latter. The view which is forced upon us by a consideration of the reactions described above is that sulphurous acid differs from sulphuric acid in containing a hydrogen atom in place of hydroxyl, as represented in the formulas $SO_2<\overset{OH}{OH}$ and $SO_2<\overset{H}{OH}$; and, further, that in sulphurous acid one hydrogen is in combination with sulphur and the other with oxygen.

CHAPTER VI.

NITROGEN DERIVATIVES OF METHANE AND ETHANE.

The simplest compounds of carbon containing nitrogen are cyanogen and hydrocyanic acid. Strictly speaking, neither can be regarded as a derivative of a hydrocarbon, unless indeed we consider hydrocyanic acid as marsh gas, in which three hydrogen atoms have been replaced by one nitrogen: $C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.$ and $C\left\{\begin{matrix}N\\H\end{matrix}\right.$. That, however, is a mere matter of words, as there is nothing in the conduct of either substance, or in the methods of formation of hydrocyanic acid, that would lead us to suspect any relation between them. Though cyanogen and hydrocyanic acid are therefore not to be considered as derivatives of the hydrocarbons, they form the starting-point for the preparation of so many important compounds that they and their simpler derivatives must receive some consideration at this stage.

Cyanogen, $(CN)_2$. — All organic compounds that contain nitrogen give sodium cyanide when ignited with sodium. So, also, potassium cyanide is formed when charcoal containing nitrogen is heated with potassium carbonate. Cyanogen itself is most readily made by heating mercuric cyanide, $Hg(CN)_2$. The decomposition that takes place is, in the main, like the simple decomposition of mercuric oxide in preparing oxygen: —

$$Hg(CN)_2 = Hg + (CN)_2;$$
$$HgO \quad = Hg + O.$$

But, in heating mercuric cyanide, a black solid substance, *paracyanogen*, is formed, and remains behind in the retort. It has the same composition as cyanogen, and although its molecular weight is not known, it is presumably a polymeric form of cyanogen.

Cyanogen (from κύανος, *blue*) owes its name to the fact that several of its compounds have a blue color. It is a colorless gas, which is easily soluble in water and alcohol, and *is extremely poisonous*. It burns with a purple-colored flame.

In aqueous solution, cyanogen soon undergoes change, and a brown amorphous body is deposited. In the solution are found hydrocyanic acid, oxalic acid, ammonia, carbon dioxide, and urea. A little dilute acid prevents this decomposition.

The compounds containing the cyanogen group, CN, may be compared with those containing the halogens. In them the cyanogen group plays the same part as the halogen atom in the halides. Thus we have: —

AgCl	AgCN
KCl	KCN
$FeCl_2$	$Fe(CN)_2$
etc.	etc.

Hydrocyanic acid, HCN. — This acid, which is commonly called *prussic acid*, occurs in nature in amygdalin in combination with other substances, in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by decomposing metallic cyanides with hydrochloric acid, as represented in the equation: —

$$KCN + HCl = KCl + HCN.$$

It can also be made by treating chloroform with ammonia: —

$$CHCl_3 + NH_3 = HCN + 3\,HCl,$$

or

$$CHCl_3 + 5\,NH_3 = NH_4.CN + 3\,NH_4Cl.$$

It is a volatile liquid, boiling at 26.5°, which solidifies at −15°. It has a very characteristic odor, suggesting bitter almonds. *It is extremely poisonous.* It dissolves in water in all proportions, and it is this solution which is known as prussic acid. Pure

hydrocyanic acid may be kept unchanged. When water or ammonia is present, it decomposes and gives ammonia, formic acid, oxalic acid, and a brown substance. By boiling with alkalies or acids, it is converted into formic acid and ammonia (see p. 56).

Hydrocyanic acid can be detected by the fact that when its solution is saturated with caustic potash, and a solution containing a ferrous and a ferric salt is added, a precipitate of Prussian blue is formed when the mixture is acidified; or, by adding yellow ammonium sulphide to its solution, evaporating to dryness, and then adding a drop of a solution of ferric chloride. If hydrocyanic acid was present, the solution turns a deep blood red in consequence of the formation of ferric sulphocyanate.

Cyanides. — Hydrocyanic, like hydrochloric acid, forms a series of salts, which are called the *cyanides*. The cyanides of the alkali metals and of mercury are soluble in water. The cyanides of the heavy metals have a marked tendency to form double cyanides, and those double cyanides which contain an alkali metal are soluble in water. Hence, the precipitates formed by potassium cyanide, in solutions containing the heavy metals, are dissolved by excess of the cyanide.

Potassium cyanide, KCN. — When potassium ferrocyanide is ignited, pure potassium cyanide is formed according to this equation: —

$$K_4Fe(CN)_6 = 4\,KCN + FeC_2 + N_2.$$

Plainly only two-thirds of the cyanogen is thus obtained in the form of the potassium salt. In order to obtain a larger yield of cyanide it has been customary to melt together potassium carbonate and ferrocyanide. The reaction that takes place is represented thus: —

$$K_4Fe(CN)_6 + K_2CO_3 = 5\,KCN + KCNO + CO_2 + Fe.$$

The product contains potassium cyanate. Potassium cyanide,

free from the cyanate, but containing sodium cyanide, is now made on the large scale by heating together dehydrated potassium ferrocyanide and metallic sodium: —

$$K_4Fe(CN)_6 + 2\,Na = 4\,KCN + 2\,NaCN + Fe.$$

Potassium cyanide is *a violent poison.* It dissolves easily in water. When the solution is boiled, ammonia and acid potassium carbonate are formed. The solution has an alkaline reaction. It is decomposed by carbon dioxide and hence has the odor of hydrocyanic acid. It precipitates almost all metallic salts, the solution in excess forming double cyanides.

Among the best-known double cyanides are the two salts, *potassium ferrocyanide* and *potassium ferricyanide.* The former is commonly called *yellow prussiate of potash,* and the latter *red prussiate of potash.*

Potassium ferrocyanide, $4\,KCN.Fe(CN)_2 + 3\,H_2O$. — This salt is made on the large scale by melting together, in iron vessels, refuse animal substances (*i.e.*, organic matter containing nitrogen) with potassium carbonate and iron. The mass is treated with water, and the salt which is thus extracted purified by crystallization.

It crystallizes in large monoclinic tables, and is soluble in about four parts of water at 15°.

Experiment 24.[1] Make a mixture of 8 parts (100g) dehydrated potassium ferrocyanide and 3 parts (60g) dry potassium carbonate. Fuse in an iron crucible, at a low red heat, until a specimen taken out and placed on a stone is white when solid. Then pour out on a flat, smooth stone, and afterwards break up and put in a dry bottle.

When treated with dilute sulphuric acid, the ferrocyanide yields hydrocyanic acid thus: —

$$2[4\,KCN.Fe(CN)_2] + 3\,H_2SO_4 = 6\,HCN + 2[KCN.Fe(CN)_2] + 3\,K_2SO_4.$$

This reaction is the one actually made use of for the preparation of hydrocyanic acid.

[1] Experiments 24 and 26 may be postponed until urea is studied, when they may be combined with the artificial preparation of urea.

Potassium ferrocyanide is the starting-point for the preparation of all compounds containing cyanogen.

Potassium ferricyanide, 3 KCN.Fe(CN)$_3$. — This salt, known as red prussiate of potash, is prepared *by oxidizing the ferrocyanide,* either by means of chlorine or of potassium permanganate.

Experiment 25. Dissolve 26^g potassium ferrocyanide in 200^{cc} cold water, and add 8^{cc} ordinary concentrated hydrochloric acid. Into this pour slowly a cold solution of 2^g of potassium permanganate in 300^{cc} water. The oxidation is complete when a drop added to ferric chloride gives a brownish-red color, but no precipitate. Neutralize with chalk, filter, and evaporate *on a water-bath.*

Potassium ferricyanide is easily soluble in water, and crystallizes from its concentrated solutions in large, dark-red rhombic prisms.

In alkaline solutions it is an excellent oxidizing agent. Reducing agents, such as hydrogen sulphide, sodium thiosulphate (hyposulphite), etc., convert it into the yellow salt.

(1) *Prussian blue,* (2) *Turnbull's blue,* and (3) *soluble Prussian blue* are complex cyanides of iron represented by the formulas

(1) $4\,Fe(CN)_3.3\,Fe(CN)_2$ or $Fe_4'''[Fe''(CN)_6]_3^{iv}$,
(2) $3\,Fe(CN)_2.2\,Fe(CN)_3$ or $Fe_3''[Fe'''(CN)_6]_2'''$, and
(3) $KCN.Fe(CN)_3.Fe(CN)_2$ or $KFe'''[Fe''(CN)_6]^{iv}$, respectively.

For a full account of the many compounds of the metals and cyanogen, the student is referred to larger works.

Cyanogen chlorides. — When chlorine is allowed to act upon cyanides or dilute hydrocyanic acid, a volatile liquid is formed which has the composition represented by the formula CNCl. It boils at 15.5°, and its vapor acts upon the eyes, causing tears. It is known as *liquid cyanogen chloride* to distinguish it from *solid cyanogen chloride.* The latter has the formula $(CN)_3Cl_3$, and is formed by treating anhydrous hydrocyanic acid with chlorine in direct sunlight. The liquid variety is partially transformed into the solid when kept in sealed tubes.

Similar compounds of cyanogen with bromine and iodine are known.

Cyanic acid, NCOH. — When a cyanide of an alkali is treated with an oxidizing agent, it takes up oxygen and is converted into a cyanate: —

$$NCK + O = NCOK.$$

Experiment 26.[1] Dehydrate slowly 125g potassium ferrocyanide in an iron pan on a gas stove; powder the dried salt and heat gently 1 to 2 hours. Fuse 75g potassium dichromate, cool, powder finely, and mix thoroughly with the ferrocyanide. Bring the warm mixture in small portions with an iron spoon into a shallow iron pan which is heated sufficiently to cause the powder to glow and turn black. Stir rapidly during the reaction. Powder the porous mass, bring it while still warm into a mixture of 450cc of 80 per cent alcohol and 50cc methyl alcohol in a litre balloon-flask and heat to boiling in a water-bath. The water in the bath should be boiling and the alcohol warm when the cyanide is made. Boil for five minutes; allow the undissolved part to settle and pour the clear solution through a plaited filter into a beaker standing in ice-water. The potassium cyanide separates as a heavy white crystalline powder. Shaking the flask in ice-water hastens the crystallization. Let the salt settle. With the mother-liquor repeat three times without delay the extraction of the black mass, boiling ten minutes each time. Filter, with the aid of a pump, each portion as soon as obtained; wash the united portions with ether; and dry in a desiccator over sulphuric acid. The ferrocyanide must be anhydrous and the work must be done rapidly. The hot alcoholic solution must be cooled rapidly to prevent decomposition of the cyanate.

Cyanic acid is readily decomposed by water yielding ammonia and carbon dioxide: —

$$NCOH + H_2O = NH_3 + CO_2.$$

The potassium salt is easily soluble in water, but is decomposed by it, yielding ammonia and potassium carbonate: —

$$NCOK + 2\,H_2O = KHCO_3 + NH_3.$$

The most interesting salt of cyanic acid is *ammonium cyanate*, $NCO.NH_4$. It can be made by adding ammonium sulphate to

[1] See Note, p. 82.

a solution of the potassium salt. It is easily soluble in water; but, if allowed to stand in solution, or if its solution is heated, *it is completely transformed into urea,* which is isomeric with it. The interest connected with this transformation was referred to in the introductory chapter (p. 1). It will be treated of more fully under urea.

Cyanuric acid, $C_3N_3H_3O_3$. — This acid bears a relation to cyanic acid similar to that which solid cyanogen chloride, $(CN)_3Cl_3$, bears to the liquid variety. It is made by treating the solid chloride with water, and also by heating urea. It is a crystallized substance.

Sulpho-cyanic acid, NCSH. — Just as the cyanides of the alkalies take up oxygen and are converted into cyanates, so also they take up sulphur and are converted into sulpho-cyanates: —

$$CNK + S = NCSK.$$

Potassium sulpho-cyanate.

Experiment 27. Mix 46g dehydrated potassium ferrocyanide with 17g dehydrated potassium carbonate, 32g sulphur, and 2g powdered charcoal. Fuse the mixture in an iron pan on a gas stove until the mass has become liquid, and a sample no longer precipitates Prussian blue when added to a solution of ferric chloride but turns the solution blood-red: —

$$K_4Fe(CN)_6 + K_2CO_3 + 8\,S = 6\,KCNS + FeS_2 + CO_2 + O.$$

The oxidation of the sulphur is prevented by the charcoal. Pour the fused mass on an iron plate, break it up into a coarse powder, and bring it into a flask with 250cc alcohol. Boil with a return condenser for 10 minutes, and finally filter the hot solution, which contains only sulphocyanate. On cooling, the salt crystallizes in long colorless prisms. Pour off the mother-liquor, and use it to extract the residue again for a second crystallization. Evaporation of the mother-liquor will yield a third crystallization. The dried crystals should be preserved in well-stoppered bottles, as the salt is very hygroscopic.

Potassium sulpho-cyanate crystallizes in long striated prisms without water of crystallization. It is deliquescent. When dissolved in water the temperature sinks markedly. When 100

parts of water of 10.8° are mixed with 150 parts of the salt, the temperature sinks to − 23.7°. By evaporation of the solution, the salt can be recovered.

Experiment 28. Dissolve some potassium sulpho-cyanate in water, and note the temperature before and after introducing the salt.

Ammonium sulpho-cyanate, $NCS.NH_4$. This salt is most easily prepared by treating carbon disulphide with concentrated alcoholic ammonia: —

$$CS_2 + 4\,NH_3 = CNS.NH_4 + (NH_4)_2S.$$

Experiment 29. Mix 240cc strong aqueous ammonia, 240cc alcohol, and 60g carbon disulphide. Allow the mixture to stand for one or more days. Then distil down to one-third of the original volume, and filter while still hot the solution left in the flask. On cooling, ammonium sulpho-cyanate will crystallize out.

The salt crystallizes in plates. It melts at 160° (try it), and at this temperature is partly transformed into the isomeric substance sulpho-urea. (Analogy to transformation of ammonium cyanate.)

Having thus considered some of the more important simpler cyanogen compounds, we may now return to the nitrogen derivatives of the hydrocarbons. For convenience, these may be divided into three classes: —

(1) *Those which are related to cyanogen;*
(2) *Those which are related to ammonia;*
(3) *Those which are related to nitric acid.*

Cyanides.

Methyl cyanide, $CH_3.CN$. — This compound is formed by distilling a mixture of potassium methyl-sulphate and potassium cyanide: —

$$\left.\begin{matrix}CH_3\\K\end{matrix}\right\rangle SO_4 + KCN = K_2SO_4 + CH_3CN.$$

It is a liquid boiling at 82°.

According to the method of preparation, it must be regarded as an ethereal salt of hydrocyanic acid, containing methyl in the place of the potassium of the potassium salt.

Ethyl cyanide, $C_2H_5.CN$. — Formed like the methyl compound. Also by heating chlor-ethane with potassium cyanide: —

$$C_2H_5Cl + KCN = C_2H_5.CN + KCl.$$

It is a liquid boiling at 98°.

The two most characteristic reactions of these cyanides are (1) that which is effected by caustic alkalies, and (2) that effected by nascent hydrogen.

When methyl cyanide is treated with caustic potash, it yields acetic acid and ammonia: —

$$CH_3.CN + H_2O + KOH = CH_3.CO_2K + NH_3.$$

This reaction is strictly analogous to that which takes place with hydrocyanic acid, yielding formic acid (see p. 56). In the same way ethyl cyanide yields an acid of the formula $C_3H_6O_2$ (or $C_2H_5.CO_2H$). Thus, by making a cyanide, we have it in our power to make an acid containing the same number of carbon atoms.

This reaction, therefore, makes it possible to pass from an alcohol to an acid containing one atom of carbon more than the alcohol contains. It has been of great service in the study of the compounds of carbon.

Note for Student. — Show how, by starting with methyl alcohol, acetic acid may be made by passing through the cyanide.

There are two ways in which the cyanogen group can be linked to methyl in methyl cyanide; viz., either by the carbon atom, as represented in the formula $H_3C - C - N$, or by the nitrogen atom, as represented thus, $H_3C - N - C$. The ease with which the nitrogen is separated from the compound, leaving the two carbon atoms united, as shown in the reaction with caustic potash, naturally leads to the conclusion that the for-

mer view is the correct one. If it is correct, it would appear to follow that in potassium cyanide the potassium is in combination with carbon as represented in the formula K — C — N, and further that in hydrocyanic acid the hydrogen is in combination with carbon, as shown thus, H — C — N.

In consequence of the close relation existing between the cyanides and the acids, the former are often called the *nitriles* of the acids. Thus methyl cyanide, which is converted into acetic acid by boiling with caustic potash, is called the nitrile of acetic acid, or *aceto-nitrile.* In the same way hydrocyanic acid itself may be regarded as the nitrile of formic acid, or *formo-nitrile.*

When methyl cyanide is treated with nascent hydrogen, it is converted into a substance which closely resembles ammonia, known as *ethyl-amine.* It will be shown to bear to ammonia the relation indicated by the formula $N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$; *i.e.*, it is ammonia in which one hydrogen has been replaced by ethyl. The reaction may be represented by the equation: —

$$H_3C - C - N + 4\,H = H_3C - H_2C - NH_2 \left[\text{ or } N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.\right].$$

This transformation strengthens the conclusion already reached, that the two carbon atoms in methyl cyanide are directly united. If this were not the case, it is difficult to see how a compound containing ethyl in which the two carbon atoms are unquestionably united, could be formed so easily from it.

Just as methyl cyanide yields ethyl-amine when treated with nascent hydrogen, so hydrocyanic acid yields methyl-amine $N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.$: —

$$H-C-N + 4\,H = H_3C-NH_2 \left[\text{ or } N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.\right].$$

The amines, or substituted ammonias, will be treated of more fully hereafter.

Isocyanides or Carbamines.

If, in making an ethereal salt of hydrocyanic acid from a salt, the silver salt is used, a compound is obtained having the same composition as the cyanide, but differing very markedly from it. The substance thus obtained is called an *isocyanide* or *carbamine.*

Ethyl isocyanide or ethyl carbamine, C_2H_5NC. — This compound is obtained when silver cyanide and iodo-ethane are heated together: —

$$C_2H_5I + AgNC = C_2H_5NC + AgI.$$

It is also formed when chloroform and ethyl-amine (see above) are brought together: —

$$CHCl_3 + N\begin{cases} C_2H_5 \\ H \\ H \end{cases} = C_2H_5NC + 3\ HCl.$$

It is a liquid boiling at 78.1°. It is characterized by an *extremely disagreeable odor.* The methyl compound obtained by the same method boils at 59.6°, but otherwise has properties almost identical with those of ethyl isocyanide.

The reactions of these substances are quite different from those of the cyanides. They are decomposed only with great difficulty by the caustic alkalies; but, when treated with dilute hydrochloric acid, they undergo an interesting change, which may be represented by the following equation for the methyl compound: —

$$CH_3NC + 2\ H_2O = \underset{\text{Methyl amine.}}{CH_3{-}NH_2} + \underset{\text{Formic acid.}}{H.CO_2H}.$$

This reaction indicates that in the isocyanides the cyanogen group is united to the radical by means of nitrogen, as represented by the formula $H_3C - N - C$. Hence it is, in all probability, that when they undergo decomposition the nitrogen

remains in combination with the radical, while the carbon of the cyanogen group passes out of the compound. The conduct of ethyl isocyanide is represented by the equation: —

$$C_2H_5.NC + 2\,H_2O = C_2H_5 - NH_2 + H.CO_2H.$$

The reactions of the cyanides and of the isocyanides, and the conclusions drawn from them, admirably illustrate the methods used in determining the structure of compounds of carbon; and they are specially valuable, as the connection between the facts and the conclusions, as expressed in the formulas, can be traced so clearly.

The fact, that the silver salt of hydrocyanic acid yields isocyanides, while the potassium and other salts yield cyanides with the halogen derivatives of the hydrocarbons, leads to the suspicion that in silver cyanide the metal may be in combination with nitrogen and not with carbon, while in the potassium salt it may be in combination with carbon. A more probable view is that the cyanides have the constitution $MN=C$. When ethyl iodide acts upon potassium cyanide, the principal reaction is direct addition: —

$$KN=C + C_2H_5I = KN=C<\begin{matrix}C_2H_5\\ I\end{matrix}.$$

If the product should break down with elimination of potassium iodide, the result would be a cyanide, $N\equiv C - C_2H_5$. In the case of silver cyanide, however, the principal action would be substitution, because of the ready combination of the silver with the iodine: —

$$AgN=C + C_2H_5I = C_2H_5N=C.$$

The product in this case would be an isocyanide.

A fact to be borne in mind in connection with the peculiar relations between the cyanides and the isocyanides is that it has been shown that some of the isocyanides are transformed into cyanides by heat.

Experiment 30. The odor of the isocyanides, as has been stated, is extremely disagreeable, and in concentrated form it is almost unbearable. A vivid impression in regard to this property may be produced by the following experiment. In a test-tube bring together a *little* chloroform, aniline, and alcoholic potash. The reaction takes place at once. It is better to perform the experiment out-of-doors, and in such a place that the tube with its contents can be thrown away without molesting any one. The aniline used is a substituted ammonia analogous to methylamine, containing the radical C_6H_5 in place of methyl. The isocyanide formed has the formula $C_6H_5.NC$.

Cyanates and Isocyanates.

There are two series of compounds bearing to cyanic acid much the same relation that the cyanides and isocyanides bear to hydrocyanic acid.

In the *cyanates*, which seem to be formed by passing cyanogen chloride into alcoholates ($CH_3ONa + CNCl = CH_3OCN + NaCl$), the radical is probably united to the cyanogen by means of oxygen, as represented in the formula CH_3-O-CN.

In the isocyanates (first called *cyanates*), on the other hand, the radical is believed to be united to the cyanogen by means of nitrogen, as represented thus, CH_3-N-CO. The isocyanates are made by distilling potassium cyanate with the potassium salt of methyl- or ethyl-sulphuric acid. They can be made also by bringing together the iodides of radicals, as iodo-methane and silver cyanate. They are very volatile substances, which have penetrating and suffocating odors.

One of the principal reactions of the cyanates is that which they undergo with caustic alkalies, hydrochloric acid, etc. They yield a cyanate and an alcohol.

The isocyanates readily yield substituted ammonias, just as the isocyanides do: —

$$C_2H_5 - N - CO + H_2O = C_2H_5.NH_2 + CO_2;$$
$$CH_3 - N - CO + H_2O = CH_3.NH_2 + CO_2.$$

The views held in regard to the structure of the cyanates and isocyanates are based upon these reactions, which, as will be

observed, are similar to those more fully presented in discussing the difference between the cyanides and isocyanides.

The existence of two cyanic acids, and of two series of salts derived from them, seems possible.

Sulpho-cyanates.

The ethereal salts of sulphocyanic acid are easily made by distilling potassium sulpho-cyanate and the potassium salt of methyl- or ethyl-sulphuric acid: —

$$\begin{matrix} CH_3 \\ K \end{matrix} > SO_4 + KSCN = CH_3SCN + K_2SO_4.$$

The ethyl compound, which is very similar to the methyl compound, is a liquid boiling at 146°.

When boiled with nitric acid, it is oxidized to ethyl-sulphonic acid. Now, it has been shown above (see p. 77), that in ethyl-sulphonic acid the ethyl in all probability is in combination with the sulphur. It hence follows that, in the sulphocyanates obtained from potassium sulphocyanate, the radical is also in combination with sulphur, as indicated in the formula, C_2H_5-S-CN. This view is supported by the fact that ethyl sulpho-cyanate readily yields ethyl mercaptan as a product of decomposition.

The sulphocyanates are converted into iso-sulpho-cyanates or mustard-oils by heat.

Iso-sulpho-cyanates or Mustard-Oils.

A number of compounds isomeric with the sulpho-cyanates are known. The best-known member of the class is ordinary *mustard-oil*. Hence they have been called *mustard-oils*, and they are generally known by this name. The mustard-oils are made by means of a series of somewhat complicated reactions, which it is rather difficult to interpret without a comparison with some similar reactions that take place between simpler substances.

When dry ammonia and dry carbon dioxide act upon each other, so-called anhydrous ammonium carbonate is formed. This is really the ammonium salt of carbamic acid, $OC<^{NH_2}_{OH}$. Its formation is represented thus: —

$$CO_2 + 2\,NH_3 = OC<^{NH_2}_{ONH_4}.$$

Now, remembering that carbon disulphide is similar to carbon dioxide, and that ethyl-amine is similar to ammonia, we can readily understand the reaction which takes place when these two substances are brought together: —

$$CS_2 + 2\,NH_2C_2H_5 = SC<^{NHC_2H_5}_{S(NH_3C_2H_5)}.$$

The product formed is the ethyl-ammonium salt of the acid $SC<^{NHC_2H_5}_{SH}$, which may be called ethyl-sulpho-carbamic acid. When the ethyl-ammonium salt is treated with silver nitrate, the corresponding silver salt, $SC<^{NHC_2H_5}_{SAg}$, is precipitated. And finally, when this salt is distilled, it breaks up, yielding *ethyl mustard-oil*, silver sulphide, and hydrogen sulphide: —

$$2\,SC<^{NHC_2H_5}_{SAg} = 2\,SC-NC_2H_5+H_2S+Ag_2S.$$

Ethyl mustard-oil is an oily liquid which does not mix with water. It has a very penetrating odor, and acts upon the mucous membranes of the eyes and nose in the same way as ordinary oil of mustard. The properties of the two are so much alike that one could be substituted for the other.

Some of the arguments have been stated which lead to the view that in the sulpho-cyanates the radical is in combination with sulphur. The reactions of the mustard-oils lead just as clearly to the conclusion that in them the radical is in combination with nitrogen. In the first place, they are made from the amines. Again, when heated with water or with hydro-

chloric acid, ethyl mustard-oil is decomposed, yielding *ethyl-amine*, carbon dioxide, and hydrogen sulphide: —

$$SC{-}NC_2H_5 + 2\ H_2O = C_2H_5.NH_2 + H_2S + CO_2.$$

And further, nascent hydrogen converts it into *ethyl-amine* and formic thioaldehyde (*i.e.*, formic aldehyde in which the oxygen has been replaced by sulphur): —

$$SC{-}NC_2H_5 + 4\ H = C_2H_5.NH_2 + H_2CS.$$

Thus, as will be seen, the tendency of the sulpho-cyanates is to yield sulphides of the radicals like ethyl sulphide, $(C_2H_5)_2S$; the tendency of the iso-sulpho-cyanates is to yield substituted ammonias, like ethyl-amine, $NH_2.C_2H_5$. These facts point to the relations expressed in the formulas, R—S—CN for the sulpho-cyanates, and R—N—CS for the iso-sulpho-cyanates or mustard-oils.

In reviewing now the compounds of the hydrocarbons which are related to the cyanogen, we see that there are two isomeric series of these, the names and general formulas of which are given below: —

Cyanides, R—C—N	Isocyanides or Carbamines,	R—NC.
Cyanates, R—O—CN	Isocyanates,	R—N—CO.
Sulpho-cyanates, R—S—CN . .	Iso-sulpho-cyanates or Mustard-oils.	R—N—CS.

Note for Student. — Study these compounds until the exact connection between the formulas and the facts above stated is clearly seen.

Substituted Ammonias.

When brom-ethane or any similar substitution-product is treated with ammonia, the reactions represented by the following equations take place step by step: —

$$C_2H_5Br + NH_3 = NH_2(C_2H_5).HBr;$$
$$C_2H_5Br + NH_2(C_2H_5) = NH(C_2H_5)_2.HBr;$$
$$C_2H_5Br + NH(C_2H_5)_2 = N(C_2H_5)_3.HBr;$$
$$C_2H_5Br + N(C_2H_5)_3 = N(C_2H_5)_4Br.$$

The first three products are salts of hydrobromic acid, and substances which closely resemble ammonia. When these salts are distilled with potassium hydroxide they are decomposed, just as ammonium bromide would be. Only instead of getting ammonia and potassium bromide, we get the compounds *ethyl-amine*, $NH_2.C_2H_5$, *di-ethyl-amine*, $NH(C_2H_5)_2$, and *tri-ethyl-amine*, $N(C_2H_5)_3$. These substances may be regarded as derived from ammonia by the replacement of one, two, and three of the hydrogen atoms respectively by ethyl. The last product of the series of reactions represented above may be regarded as ammonium bromide, NH_4Br, in which all four hydrogen atoms are replaced by ethyl groups.

The decomposition by potassium hydroxide of the first two salts is represented thus: —

$$NH_2(C_2H_5).HBr + KOH = NH_2(C_2H_5) + KBr + H_2O;$$
$$NH(C_2H_5)_2.HBr + KOH = NH(C_2H_5)_2 + KBr + H_2O.$$

Methyl-amine, $NH_2.CH_3$. — This compound can be prepared by treating iodo-methane with ammonia: —

$$CH_3I + NH_3 = NH_2CH_3.HI.$$

It was first made by treating methyl isocyanate, CH_3-N-CO, with caustic potash: —

$$CH_3 - N - CO + H_2O = NH_2.CH_3 + CO_2.$$

It has been stated that it is formed by treating hydrocyanic acid with nascent hydrogen: —

$$HCN + 4H = NH_2.CH_3.$$

It occurs in nature in herring brine, in *Mercurialis perennis*, and is one of the products of the distillation of animal matter as well as of wood.

Methyl-amine is a gas which is easily condensed to a liquid. It smells like ammonia. It is, like ammonia, extremely easily soluble in water, 1 volume of water at 12.5° taking up 1150 volumes of the gas. This solution acts almost exactly like a solution of ammonia in water. It is strongly alkaline. In fact, it is more strongly basic than ammonia. It precipitates the metallic hydroxides, but, unlike ammonia, it does not dissolve precipitated hydroxides of nickel, cobalt, and cadmium when added in excess. Like ammonia, it dissolves aluminium hydroxide.

Methyl-amine forms salts with acids in the same way that ammonia does; that is, by direct addition. The action towards nitric and sulphuric acids takes place in accordance with the following equations: —

$$NH_2CH_3 + HNO_3 = NH_3CH_3.NO_3;$$

$$2\,NH_2CH_3 + H_2SO_4 = (NH_3CH_3)_2SO_4.$$

These salts are called methyl-ammonium nitrate and methyl-ammonium sulphate respectively.

Di-methyl-amine, $NH(CH_3)_2$. — This is formed by heating iodo-methane with alcoholic ammonia: —

$$2\,CH_3I + 2\,NH_3 = NH(CH_3)_2.HI + NH_4I.$$

It is formed, together with methyl-amine, as a product of the distillation of wood.

It is a gas which condenses to a liquid at + 7.2°. Its properties are much like those of methyl-amine.

Tri-methyl-amine, $N(CH_3)_3$. — Tri-methyl-amine is formed as one of the products of the treatment of iodo-methane with

ammonia. It occurs widely distributed in nature, as in the blossoms of the hawthorn, the wild cherry, and the pear. It is contained in herring brine, and is a common product of the decomposition of organic substances which contain nitrogen. It is now obtained in large quantities from the so-called "vinasses." These are the waste liquids obtained in the refining of beet sugar. When the "vinasses" are evaporated to dryness, tri-methyl-amine is given off among the volatile products. It is collected as the hydrochloric acid salt, $N(CH_3)_3.HCl$, which, when heated to 260°, yields ammonia, tri-methyl-amine, and chlor-methane: —

$$3\,N(CH_3)_3.HCl = 2\,N(CH_3)_3 + NH_3 + 3\,CH_3Cl.$$

The chlor-methane is utilized for the purpose of producing low temperatures.

Tri-methyl-amine is a liquid boiling at 9° to 10°. It has a strong ammoniacal and fishy odor. It is very soluble in water and alcohol, and is a strong base.

The ethyl-amines are very much like the methyl compounds, and hence need not be specially described.

When tri-ethyl-amine is brought together with iodo-ethane, the two unite, forming the compound tetra-ethyl-ammonium iodide, $N(C_2H_5)_4I$, which is ammonium iodide, in which all four hydrogen atoms have been replaced by ethyl groups. If silver oxide is added to the aqueous solution of the iodide, silver iodide is precipitated, and by evaporation of the liquid crystals of *tetra-ethyl-ammonium hydroxide*, $N(C_2H_5)_4OH$, are obtained. This is plainly the hypothetical ammonium hydroxide, in which the four ammonium hydrogens have been replaced by ethyl. *Its solution acts almost like caustic potash.* It is very caustic, attracts carbon dioxide from the air, saponifies (see p. 70) ethereal salts, and gives the same precipitates as caustic potash. It is so strong a base that neither potassium nor sodium hydroxide can separate it from its salts. The reactions of the substituted ammonias above described make it certain that

these bodies are very closely related to ammonia. The methods of formation also point clearly to the same conclusion. This relation is best expressed by the formulas above given.

Another method for the formation of substituted ammonias in which but one radical is present, as ethyl-amine, $NH_2.C_2H_5$, or in general $NH_2.R$, consists in treating with nascent hydrogen compounds known as *nitro compounds*, which are substitution-products containing the group NO_2 in the place of hydrogen. Thus, for example, when nitro-methane, $CH_3.NO_2$ (which see), is treated with hydrogen, the reaction which takes place is represented thus: —

$$CH_3.NO_2 + 6\,H = CH_3.NH_2 + 2\,H_2O.$$

In connection with another series, it will be shown that this reaction is a most important one, from a practical as well as a scientific point of view. It may be said in anticipation that the manufacture of aniline, and consequently of all the many valuable dye-stuffs related to aniline, is based upon this reaction.

Just as we may look upon methyl-amine and the related compounds, as ammonia, in which one hydrogen atom is replaced by methyl, so also we may regard them, and with equal right, as marsh gas, in which hydrogen has been replaced by the group or residue NH_2. Owing to the frequency of the occurrence of this group in carbon compounds, and for the sake of simplifying the nomenclature, the group has been called the *amino* group, and the bodies containing it *amino-compounds*. Thus the compound $NH_2.C_2H_5$ may be called either *ethyl-amine* or *amino-ethane*, etc.

Similarly, those bodies which contain two hydrocarbon residues, as di-ethyl-amine, $NH(C_2H_5)_2$, are called *imino-compounds*, and the group NH the *imine* or *imino* group. Substituted ammonias containing one hydrocarbon residue are called *primary ammonia bases*. Those containing two residues, as di-

ethyl-amine, $NH(C_2H_5)_2$, are known as *secondary ammonia bases*, and those containing three residues, as tri-ethyl-amine, $N(CH_3)_3$, are called *tertiary ammonia bases.*

Among the most important of the reactions of amino-compounds or primary bases is that which takes place when they are treated with nitrous acid. Take ethyl-amine as an illustration. In order to understand what takes place when this compound is treated with nitrous acid, it is necessary to keep in mind the fact that the compound itself is a modified ammonia, and hence we may expect that its reactions will be but modifications of those which take place with ammonia. Thus with nitrous acid ammonia unites directly to form ammonium nitrite: —

$$NH_3 + HNO_2 = NH_4.NO_2.$$

So also ethyl-amine forms ethyl-ammonium nitrite: —

$$NH_2.C_2H_5 + HNO_2 = NH_3(C_2H_5).NO_2.$$

Ammonium nitrite breaks up readily into free nitrogen and water: —

$$NH_4.NO_2 = N_2 + H_2O + H_2O.$$

So also ethyl-ammonium nitrite breaks up into free nitrogen, water, and *alcohol:* —

$$NH_3(C_2H_5)NO_2 = N_2 + H_2O + C_2H_5.OH.$$

The two reactions are strictly analogous. As in the second case we start with a substituted ammonia, we get as a product a *substituted water* or alcohol.

This reaction has been used very extensively in the preparation of compounds containing hydroxyl. For ordinary alcohol, as is clear, it is not a convenient method of preparation; but it will be shown that there are hydroxides for the preparation of which it is by far the most convenient method. The essential character of the transformation effected by it will be best understood by comparing the formulas of the amino compound and the alcohol. We have ethyl-amine, $C_2H_5.NH_2$, and from it we

get alcohol, $C_2H_5.OH$. Thus we see that the transformation consists in replacing the amino group by hydroxyl.

Hydrazine Compounds.

There is an important class of compounds, the members of which bear the same relation to the compound hydrazine, N_2H_4 ($H_2N - NH_2$), that the substituted ammonias bear to ammonia. The reactions by which they are prepared are somewhat complicated, and cannot well be discussed at this stage. The best-known hydrazines are those related to the hydrocarbons of the benzene series, as, for example, phenylhydrazine, $C_6H_5.NH.NH_2$.

Nitro-Compounds.

Reference has already been made to a class of compounds containing the group NO_2, and known as nitro-compounds. They are most readily made by treating the hydrocarbons with nitric acid. This method, however, is not applicable to the hydrocarbons methane and ethane and their homologues, as these are not readily changed by nitric acid. The hydrocarbon benzene, C_6H_6, is very easily acted upon by nitric acid, when the reaction represented by the following equation takes place: —

$$C_6H_6 + HO.NO_2 = C_6H_5.NO_2 + H_2O.$$

The action is like that which takes place between sulphuric acid and benzene, which gives the sulphonic acid $C_6H_5.SO_2OH$ or $\begin{matrix} C_6H_5 \\ HO \end{matrix} > SO_2$. (See p. 76.) In each case a hydroxyl of the acid is replaced by the simple residue of the hydrocarbon. The product in the case of the dibasic acid, sulphuric acid, is itself still acid, while the product in the case of the monobasic nitric acid, is not an acid.

The nitro-derivatives of methane have been made by a reaction which we should expect to yield ethereal salts of nitrous acid; namely, by treating iodo-methane or ethane with silver nitrite: —

$$CH_3I + AgNO_2 = CH_3NO_2 + AgI.$$

The compound $CH_3.NO_2$, which is known as *nitro-methane*, does not conduct itself like the ethereal salts of nitrous acid. Methyl nitrite, $CH_3O.NO$, can be saponified; nitro-methane cannot.

NOTE FOR STUDENT. — Compare the reaction just referred to with that which takes place between silver cyanide and iodo-methane; and that which takes place between iodo-ethane and potassium sulphite. What analogy is there to the former and to the latter?

It has already been stated that the nitro-derivatives are converted by nascent hydrogen into the corresponding amino-derivatives (see p. 98).

NOTE FOR STUDENT. — Write the equations representing the reactions necessary to convert methyl alcohol into methyl-amine by means of the nitro-compound.

Nitroform, $CH(NO_2)_3$, as the formula indicates, is the tri-nitro-derivative of methane, or tri-nitro-methane. It is converted into *tetra-nitro-methane*, $C(NO_2)_4$, when treated with a mixture of concentrated sulphuric and fuming nitric acids.

Nitro-chloroform, $C(NO_2)Cl_3$, called also *chlorpicrin* and *nitro-trichlormethane*, is formed by distilling methyl or ethyl alcohol with common salt, saltpetre, and sulphuric acid. It is formed from a number of more complicated nitro-compounds, by distilling them with bleaching lime or hydrochloric acid and potassium chlorate.

NITROSO- AND ISONITROSO-COMPOUNDS.

When a compound containing the group CH is treated with nitrous acid, a reaction takes place, which is represented thus: —

$$R_3.CH + HO.NO = R_3.C.NO + H_2O.$$

The product $R_3.C.NO$, which is derived from the original substance by the substitution of the group NO for a hydrogen atom, is called a *nitroso-compound*. By oxidation the nitroso-

compounds are converted into nitro-compounds, and by reduction they yield the same products as the corresponding nitro-compounds, that is to say, the amines.

The isonitroso-compounds are isomeric with the nitroso-compounds. They are formed when acetones or aldehydes are treated with hydroxylamine, $NH_2.OH$. The reaction may be represented thus: —

$$\begin{array}{l} CH_3 \\ | \\ CO + H_2N.OH = \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ C = N - OH + H_2O. \\ | \\ CH_3 \end{array}$$

The hydrogen of the hydroxyl has acid properties. The isonitroso-compounds are readily broken up by hydrochloric acid, yielding, as one of the products, hydroxylamine. They are generally called *oximes*.

As hydroxylamine reacts in this way with all aldehydes and with all ketones, it is a valuable reagent for compounds belonging to these classes.

Fulminic acid, CNOH, according to recent investigations, appears to be an isonitroso-compound, and for that reason finds appropriate mention in this place. The principal compound of fulminic acid, is the mercury salt, $C_2N_2O_2Hg$, commonly known as *fulminating mercury*. It is prepared by dissolving mercury in strong nitric acid, and adding alcohol to the solution. It is extremely explosive. Mixed with potassium nitrate it is used for filling percussion-caps.

When fulminating mercury is treated with concentrated hydrochloric acid, it yields hydroxylamine as one of the products of decomposition. Fulminic acid appears, therefore, to be an isonitroso-compound. It is probably the oxime of carbon monoxide, and should be represented by the formula $C = N - OH$. As will be seen, fulminic acid is isomeric with cyanic and cyanuric acids (see pp. 84 and 85).

CHAPTER VII.

DERIVATIVES OF METHANE AND ETHANE CONTAINING PHOSPHORUS, ARSENIC, ETC.

Phosphorus compounds.—Corresponding to the amines or substituted ammonias are the phosphines, which, as the name implies, are related to phosphine, PH_3. Methyl-phosphine, $PH_2.CH_3$, di-methyl-phosphine, $PH(CH_3)_2$, and tri-methyl-phosphine, $P(CH_3)_3$, may be taken as examples.

These substances, like the corresponding amines, form salts with acids, though not as readily. The hydroxide, *tetra-ethyl-phosphonium hydroxide*, $P(C_2H_5)_4.OH$, is a very strong base, though not as strong as the corresponding nitrogen derivative.

The phosphines have one marked property which distinguishes them from the amines, and that is their power to take up oxygen and form acids. Thus, ethyl-phosphine, $PH_2.C_2H_5$, when treated with nitric acid, is converted into *ethyl-phosphinic acid*, $PO(C_2H_5)(OH)_2$, a dibasic acid, bearing to phosphoric acid the same relation that the *sulphonic* acids bear to sulphuric acid.

NOTE FOR STUDENT.—What is the relation? What other class of acids bears the same relation to carbonic acid?

Di-ethyl-phosphine, $PH(C_2H_5)_2$, yields *di-ethyl-phosphinic acid*, $PO(C_2H_5)_2.OH$, when oxidized.

These compounds are not commonly met with, and do not play a very important part in the study of the compounds of carbon.

Arsenic compounds.—The most characteristic carbon compound containing arsenic is that which is known as *cacodyl*,

a name given to it on account of its extremely disagreeable odor (from κακώδης, *stinking*). It is prepared by distilling a mixture of potassium acetate and arsenic trioxide. The reactions which take place are very complicated, and many products are formed. Chief among the products is *cacodyl oxide*: —

$$4\ CH_3.CO_2K + As_2O_3 = [\ (CH_3)_2As]_2O + 2\ K_2CO_3 + 2\ CO_2.$$

When treated with hydrochloric acid, the oxide is converted imto the *chloride* $(CH_3)_2AsCl$; and, when the chloride is treated with zinc, cacodyl itself is produced. Its analysis and the determination of its molecular weight lead to the formula $As_2C_4H_{12}$, which in all probability should be represented thus: $\left.\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\right\}$. Cacodyl appears thus as a compound analogous to the hydrazines referred to above. (See p. 100.)

Note for Student.— In what does the analogy consist ?

Many derivatives of cacodyl have been made, but their study would hardly be profitable at this stage.

Zinc ethyl itself is made by treating iodo-ethane, C_2H_5I, with zinc alone or with zinc sodium. The reaction takes place in two stages. First by addition, a compound of the formula $Zn<\begin{matrix}I\\C_2H_5\end{matrix}$ is formed. When this is distilled, zinc ethyl and zinc iodide are formed: —

$$2\ Zn<\begin{matrix}I\\C_2H_5\end{matrix} = Zn(C_2H_5)_2 + ZnI_2.$$

It is a liquid boiling at 118°. It takes fire in the air, and burns with a white flame.

Sodium ethyl, C_2H_5Na, can be obtained in combination with zinc ethyl by treating the latter with sodium. Both these compounds have been used to a considerable extent in the synthesis of carbon compounds, particularly the more complex hydrocarbons, and they will be frequently referred to in the following pages.

NOTE FOR STUDENT. — What is formed when sodium methyl and carbon dioxide are allowed to act upon each other?

Many of the derivatives, like the above, are volatile liquids. Such, for example, are mercury ethyl, $Hg(C_2H_5)_2$, aluminium ethyl, $Al(C_2H_5)_3$, tin tetrethyl, $Sn(C_2H_5)_4$, and silicon tetrethyl, $Si(C_2H_5)_4$. The study of these compounds has been of assistance in enabling chemists to determine the atomic weights of some of the elements which do not form simple volatile compounds.

RETROSPECT.

In the introductory chapter (p. 19) these words were used in describing the plan to be followed: "Of the first series of hydrocarbons *two* members will be considered. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series and of other series. Their characteristics and their relations to the hydrocarbons will be dwelt upon, as well as their relations to each other. Thus, by a comparatively close study of two hydrocarbons and their derivatives, we may acquire a knowledge of the principal classes of the compounds of carbon. After these typical derivatives have been considered, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members."

In accordance with the plan thus sketched we have thus far studied the principal derivatives of the two hydrocarbons, methane and ethane, so far as these derivatives represent distinct classes of compounds. These derivatives were classified first into (1) those containing halogens; (2) those containing oxygen; (3) those containing sulphur; and (4) those containing nitrogen. On examining each of these classes more closely, we found that the halogen derivatives, such as chlor-methane, brom-ethane, etc., bear very simple relations to each other.

We found that under the head of oxygen derivatives, the most important and most distinctly characteristic derivatives of hydrocarbons are met with; as, the *alcohols*, *ethers*, *aldehydes*, *acids*, *ethereal salts*, and *ketones*. The sulphur derivatives, some of which closely resemble the oxygen derivatives, include the *sulphur alcohols* or *mercaptans*, *sulphur ethers*, and *sulphonic acids*.

On beginning the consideration of the nitrogen derivatives we found it desirable first to take up certain derivatives containing the cyanogen group, among which are cyanogen, hydrocyanic acid, cyanic acid, and sulphocyanic acid. Many interesting carbon compounds are closely related to these fundamental compounds. Such, for example, are the *cyanides* and *isocyanides*, the *cyanates* and *isocyanates*, the *sulpho-cyanates* and *iso-sulpho-cyanates* or *mustard-oils*. Following the compounds related to cyanogen, we took up the interesting compounds which are related to ammonia, the *substituted ammonias* or *amines*. Then came the *nitro-derivatives;* and, finally, the compounds of the hydrocarbon residues or radicals with metals.

It is of the greatest importance that the student should master the preceding portion of this book. If he studies carefully the reactions that have been treated of, which are statements in chemical language that tell us the conduct of the various classes of derivatives, and if he performs the experiments which have been described, he will have a fair general knowledge of the kinds of relations which are met with in connection with the compounds of carbon through the whole field. As stated in the Introduction: "If we know what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon."

The more the student practises the use of the equations thus far given, the better he will be prepared to follow the remaining portions of the book. Indeed, it may be said that, if he thoroughly understands what has gone before, what follows will appear extremely simple. Whereas, if he has failed at any

point to catch the exact meaning, if he has failed to see the connection, he had better go back and faithfully review, or he will soon find his mind hopelessly muddled, and relations which are as clear as day will be concealed from him.

An excellent practice is to trace connections between the different classes of compounds, and show how to pass from one to the other. Thus, for example, (1) show by what reactions it is possible to pass from marsh gas to acetic acid. (2) How can we pass from ordinary alcohol to ethylidene chloride, $CH_3.CHCl_2$? (3) What reactions would enable us to make methyl-amine from its elements? (4) How can acetone be made from methyl-amine? (5) What reactions are necessary in order to make ordinary ether from ethyl-amine? etc., etc. It is well in this sort of practice to select what appear to be the least closely-related compounds, and to show then how we can pass from one to the other. Be sure to select representatives of all the classes hitherto mentioned, and to bring in all the important reactions.

CHAPTER VIII.

THE HYDROCARBONS OF THE MARSH-GAS SERIES, OR PARAFFINS.

The existence of the homologous series of hydrocarbons beginning with methane and ethane was spoken of before its first two members were considered. A general idea of the extent of the series, and of the names used to designate the members, may be gained from the following table: —

MARSH-GAS HYDROCARBONS.

Paraffins. — Hydrocarbons, C_nH_{2n+2}.

		Boiling-Point.
Methane	CH_4	gas.
Ethane	C_2H_6	gas.
Propane	C_3H_8	gas.
Butane (normal)	C_4H_{10}	1°.
Pentane "	C_5H_{12}	37°.
Hexane "	C_6H_{14}	69°.
Heptane "	C_7H_{16}	98°.
Octane "	C_8H_{18}	125°.
Nonane "	C_9H_{20}	150°.
Dodecane "	$C_{12}H_{26}$	214°.
Hexadecane "	$C_{16}H_{34}$	287°.

The explanation of the remarkable relation in composition existing between these members, a relation to which the name *homology* is given, has already been referred to (p. 22). The number of hydrogen atoms contained in a member of this series

bears a constant relation to the number of carbon atoms, as expressed in the general formula C_nH_{2n+2}. On examining the column headed "Boiling Point" it will be seen that, as we pass upward in the series, the boiling-point becomes higher and higher. The first three members are gases at ordinary temperatures, while the last boils at 287°. The elevation in the boiling-point is to some extent regular, as will be observed. The difference between butane, C_4H_{10}, and pentane, C_5H_{12}, is $37 - 1 = 36°$; that between pentane and the next member is $69 - 37 = 32°$; between hexane and heptane it is $98 - 69 = 29°$; between heptane and octane, $125 - 98 = 27°$; and, finally, between octane and nonane the difference is $150 - 125 = 25°$. Thus it will be seen that the elevation in boiling-point caused by the addition of CH_2 decreases as we pass upward in the series. Other relations have been pointed out, but it would be premature to discuss them here.

The chief natural source of the paraffins is petroleum; but although this substance, which occurs in such enormous quantities in nature, undoubtedly contains a number of the members of the paraffin series, it is an extremely difficult matter to isolate them from the mixture. Prolonged fractional distillation is not sufficient for the purpose. If, however, some of the purest products which can thus be obtained are treated with concentrated sulphuric acid, and afterwards with concentrated nitric acid, and then washed and redistilled, they can be obtained in pure condition.

Petroleum. — Petroleum occurs in enormous quantities in several places. Among the most important localities are Pennsylvania, the Crimea, the Caucasus, Persia, Burmah, China, etc. In some places it issues constantly from the earth. Usually it is necessary to bore for it. When one of the cavities in which it is contained is punctured, the oil is forced out of a pipe inserted into the opening in a jet, in consequence of the pressure exerted upon its surface. As

first obtained, it is usually a dark, yellowish-green liquid, with an unpleasant odor. It varies in appearance according to the place where it is found. American petroleum contains the lowest members of the paraffin series; and when the oil is exposed to the air the gases are given off.

Refining of petroleum. To render petroleum fit for use in lamps, it is necessary that the volatile portions should be removed, as they form explosive mixtures with air, just as marsh gas does. It is also necessary to remove the higher boiling portions, because they are semi-solid, and would clog the wicks of the lamps. The crude oil is therefore subjected to distillation, and only those parts which have a certain specific gravity or boil between certain points are used for illuminating purposes, under the name of *kerosene*. Besides being distilled, the oil must further be treated with concentrated sulphuric acid, which removes a number of undesirable substances, and afterwards with an alkali, and then with water. All these processes taken together constitute what is called the refining of petroleum. In the distillation, the lighter products are usually divided into several parts, according to the specific gravity or boiling-point. Thus we have the products *cymogene*, *rhigolene*, *gasoline*, *naphtha*, and *benzine*, all of which are lighter than kerosene. It must be distinctly understood that the substances here mentioned are not pure chemical individuals. The names are commercial names, each of which applies to a complex mixture of hydrocarbons. From the heavier products, that is, those that boil at higher temperatures than the highest limit for kerosene, *paraffin*, which is a mixture of the highest members of this series, is made.

Owing to the danger attendant upon the use of improperly refined petroleum, laws have been enacted relating to the properties which the kerosene exposed for sale must have. These laws, which differ somewhat in different countries and different parts of the same country, relate mostly to what is called the *flashing-point*. This is the temperature to which the

oil must be heated before it takes fire when a flame is applied to it. The legal flashing-point in many parts of the United States is 44°. A simple and accurate instrument for determining the flashing-point is here described: The cylinder *A* is at least 2.5^{cm} in diameter, and at least 16^{cm} long. Just within the cork the bent tube contracts to a small orifice. At *d* it is connected with a hand-bellows or a gas-holder; and the flow of air is controlled by a pinch-cock. The cylinder is filled with oil to a point such that, when the air is running, the surface of the foam is about 5^{cm} from the top; and it is then put in a beaker of water to the level of the oil. Air is now passed through *dcb*, and *e* so adjusted that about 0.5^{cm} foam is kept on the surface of the oil. From degree to degree the test is made by bringing a small flame for an instant to the mouth of *A*. At the flashing-point the vapor ignites, and the bluish flame runs down to the surface of the oil.

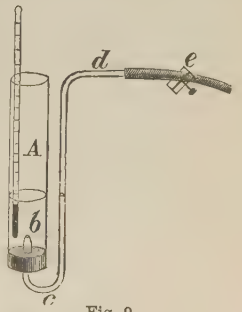


Fig. 9.

Experiment 31. Make an apparatus like the above, and determine the flashing-points of two or three specimens of kerosene that may be available.

Synthesis of the paraffins. — Although the paraffins occur in nature, and a few of them can be obtained in pure condition from natural sources, we are dependent upon synthetical operations performed in the laboratory for our knowledge of the series and the relations existing between them.

We have already seen how ethane can be prepared from methane by treating methyl iodide with zinc or sodium, as represented in this equation: —

$$CH_3I + CH_3I + 2\ Na = C_2H_6 + 2\ NaI.$$

This method has been extensively used in the building up of higher members of the series. Thus from ethane we can make ethyl iodide, and by treating this with sodium get butane C_4H_{10}: —

$$C_2H_5I + C_2H_5I + 2\ Na = C_4H_{10} + 2\ NaI.$$

But we can get the intermediate member, propane, C_3H_8, by mixing methyl iodide and ethyl iodide and treating the mixture with sodium: —

$$CH_3I + C_2H_5I + 2\ Na = CH_3.C_2H_5 + 2\ NaI.$$

By applying this method, it is plain that a large number of the members of the paraffin series might be made.

Another method consists in treating the zinc compounds of the radicals, like zinc ethyl, $Zn(C_2H_5)_2$, with the iodides of radicals. Thus zinc methyl and methyl iodide give ethane; zinc ethyl and ethyl iodide give butane; zinc ethyl and methyl iodide give propane, etc.: —

$$Zn(CH_3)_2 + 2\ CH_3I = 2\ C_2H_6 + ZnI_2;$$
$$Zn(C_2H_5)_2 + 2\ C_2H_5I = 2\ C_4H_{10} + ZnI_2;$$
$$Zn(C_2H_5)_2 + 2\ CH_3I = 2\ C_3H_8 + ZnI_2.$$

Paraffins can be made by replacing the halogen in a substitution-product by hydrogen. This can be effected by nascent hydrogen or by hydriodic acid: —

$$C_4H_9I + 2\ H = C_4H_{10} + HI.$$

As these halogen substitution-products can easily be made from the alcohols, it follows that the hydrocarbons can be made from the corresponding alcohols. Finally, the paraffins can be made by heating the acids of the formic acid series with an alkali. This has been illustrated by the preparation of marsh gas from acetic acid by heating with lime and caustic potash. The reaction may be written thus: —

$$CH_3.CO_2K + KOH = CH_4 + CO_3K_2.$$

The products are a hydrocarbon and a carbonate.

Isomerism among the paraffins. — It has already been stated that the evidence is almost conclusive that each of the four hydrogen atoms of marsh gas bears the same relation to the carbon, and hence we believe that, as regards the nature of the product, it makes no difference which hydrogen atom is replaced by a given atom or radical. According to this, as ethane is the methyl derivative of marsh gas, it makes no difference which of the hydrogen atoms of marsh gas is replaced by the methyl, the product must always be the same, or *there is but one ethane possible according to the theory.* This is represented by the formula,

$$\begin{array}{c} \mathrm{H} \quad \mathrm{H} \\ | \quad\;\; | \\ \mathrm{H}-\mathrm{C}-\mathrm{C}-\mathrm{H} \\ | \quad\;\; | \\ \mathrm{H} \quad \mathrm{H} \end{array}, \text{ or } \mathrm{H_3C-CH_3}.$$

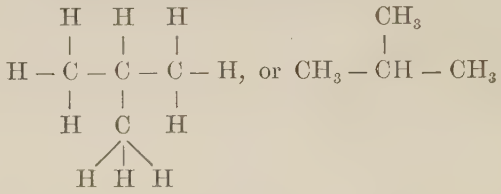
In ethane, as well as in methane, all the hydrogen atoms bear the same relation to the molecule, and it should make no difference which one is replaced by methyl. But propane is regarded as derived from ethane by the substitution of methyl for hydrogen; and, as it makes no difference which hydrogen is replaced, *there is but one propane possible.* Only one has ever been discovered, and this must be represented thus: —

$$\begin{array}{c} \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \\ | \quad\;\; | \quad\;\; | \\ \mathrm{H}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{H} \\ | \quad\;\; | \quad\;\; | \\ \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \end{array}, \text{ or } \mathrm{CH_3.CH_2.CH_3}.$$

Now, continuing the process of substitution of methyl for hydrogen, it appears that the theory indicates the possibility of the existence of two compounds of the formula C_4H_{10}. One of these should be obtained by substituting methyl for one of the three hydrogens of either methyl group of propane. It is represented by the formula: —

$$\begin{array}{c} \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \\ | \quad\;\; | \quad\;\; | \quad\;\; | \\ \mathrm{H}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{H} \\ | \quad\;\; | \quad\;\; | \quad\;\; | \\ \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \end{array}, \text{ or } \mathrm{H_3C.CH_2.CH_2.CH_3}.$$

The other should be obtained by substituting methyl for one of the two hydrogens of the group CH_2 contained in propane. This would give a hydrocarbon of the formula: —



The theory then indicates the existence of two butanes. How about the facts? Two, and only two, butanes have been discovered. The first, which occurs in American petroleum, has been made synthetically by treating ethyl iodide with zinc: —

$$2\,CH_3.CH_2I + Zn = CH_3.CH_2.CH_2.CH_3 + ZnI_2.$$

The method of synthesis clearly shows which of the two possible isomerides the product is. It is known as **normal butane**. It is a gas that can be condensed to a liquid at $+1°$.

The second, or **isobutane**, is made from an alcohol which will be shown to have the structure represented by the formula

$CH_3-C(CH_3)_2-OH$ (see Tertiary Butyl Alcohol, p. 124), by replacing the hydroxyl by hydrogen. It is a gas that becomes liquid at $-17°$.

The differences between the two butanes are observed principally in their derivatives.

Applying the same method of reasoning to the next member of the series, how many isomeric varieties of pentane, C_5H_{12}, may we expect to find? The question resolves itself into a determination of the number of kinds of hydrogen atoms contained in the two butanes, or the number of relations to the molecule represented among the hydrogen atoms of the butanes.

We can make this determination best by examining the structural formulas. Take first normal butane : —

$$\begin{array}{c} H\ \ H\ \ H\ \ H \\ |\ \ \ |\ \ \ |\ \ \ | \\ H-C-C-C-C-H. \\ |\ \ \ |\ \ \ |\ \ \ | \\ H\ \ H\ \ H\ \ H \end{array}$$

In this there are plainly two different relations represented; viz., that of each of the six hydrogens in the two methyl groups, and that of each of the four hydrogens of the two CH_2 groups. The two possible methyl derivatives of a hydrocarbon of this formula are therefore to be represented thus : —

$$H_3C.CH_2.CH_2.CH_2.CH_3, \qquad (1)$$

and

$$H_3C.CH_2.CH\begin{array}{l}CH_3\\CH_3\end{array}. \qquad (2)$$

Now, taking isobutane, $\begin{array}{l}CH_3\\|\\HC-CH_3\\|\\CH_3\end{array}$, we see that it consists of three methyl groups, giving nine hydrogen atoms of the same kind, and one CH group, the hydrogen of which bears a different relation to the molecule from that which the other nine do. There are therefore two possible methyl derivatives of isobutane which must be represented thus : —

$$\begin{array}{l}CH_3\\|\\HC-CH_2.CH_3\\|\\CH_3\end{array} \qquad (3), \qquad \text{and} \quad \begin{array}{l}\ \ CH_3\\\ \ |\\H_3C-C-CH_3.\\\ \ |\\\ \ CH_3\end{array} \qquad (4)$$

We have, therefore, apparently four pentanes. But on comparing formulas (2) and (3), it will be seen that, though written a little differently, they really represent one and the same compound. Thus the number of pentanes, the existence of which is indicated by the theory, is three, and these are represented

by formulas (1), (2), and (4). *They are all known.* The first is called **normal pentane,** the second **iso-pentane** or **di-methyl-ethyl-methane,** and the third **tetra-methyl-methane.**

¶ It would lead too far to discuss all the methods of preparation and the properties of these hydrocarbons. It will be seen that the methods of preparation show what the structure of a hydrocarbon is. Di-methyl-ethyl-methane is made from an alcohol which can be shown to have the formula

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.CH_2OH,$$

by replacing the hydroxyl by hydrogen. Hence its structure is that represented above by formulas (2) and (3).

Tetra-methyl-methane is made by starting with acetone. Acetone has been shown to consist of carbonyl in combination with two methyl groups, as represented in the formula $CH_3-CO-CH_3$. It has also been shown that, by treating acetone with phosphorus pentachloride, the oxygen is replaced by chlorine, giving a compound of the formula $CH_3-CCl_2-CH_3$. Now, by treating this chloride with zinc-methyl, the chlorine is replaced by methyl thus: —

$$CH_3-CCl_2-CH_3 + Zn(CH_3)_2 = CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3 + ZnCl_2.$$

The product is tetra-methyl-methane, and the synthesis thus effected shows at once what the structure of the product is.

Hexanes. — The student will now be prepared to apply the theory to the determination of the number of hexanes possible. He will find that there are five. The theory is, in this case as in the preceding, in perfect accordance with the facts. There are five and only five hexanes known. Only the names and formulas of these will be given here: —

1. **Normal hexane,** $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$.

2. **Iso-hexane,** $CH_3.CH_2.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}$.

3. **Methyl-di-ethyl-methane,** $CH_3.CH<\begin{matrix}CH_2.CH_3\\CH_2.CH_3\end{matrix}$.

4. **Tetra-methyl-ethane,** $\begin{matrix}H_3C\\H_3C\end{matrix}>HC-CH<\begin{matrix}CH_3\\CH_3\end{matrix}$.

5. **Tri-methyl-ethyl-methane,** $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2.CH_3$.

Passing upward, we find that *nine* heptanes are possible according to the theory, while but *five* have thus far been discovered; and that, while theory indicates the possibility of the discovery of *eighteen* hydrocarbons of the formula C_8H_{18}, but *two* are known. The theoretical number of isomeric varieties of the highest members of the series is very great, but our knowledge in regard to these highest members is very limited, and it is impossible to say whether the theory will ever be confirmed by facts. It may be that there is some law limiting the number of complicated hydrocarbons. It is, however, idle to speculate upon the subject. It is well for us to keep in mind that a thorough knowledge of a few of the simplest members of the series is all that is necessary for the present.

On examining the formulas used to express the structure of the hydrocarbons, we find that they can be divided into three classes: —

(1) Those in which there is no carbon atom in combination with more than two others; as, —

Propane . . . . $CH_3.CH_2.CH_3$;

Normal butane . . $CH_3.CH_2.CH_2.CH_3$;

Normal pentane . $CH_3.CH_2.CH_2.CH_2.CH_3$;

and Normal hexane . . $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$.

(2) Those in which there is at least one carbon atom in combination with three others; as,—

Isobutane . . . . $CH_3.CH<\begin{matrix}CH_3\\CH_3\end{matrix}$;

Isopentane . . . $CH_3.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}$;

Isohexane . . . . $CH_3.CH_2.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}$;

and Tetra-methyl-ethane, $\begin{matrix}H_3C\\H_3C\end{matrix}>CH-CH<\begin{matrix}CH_3\\CH_3\end{matrix}$.

(3) Those in which there is at least one carbon atom in combination with four others; as,—

Tetra-methyl-methane . . $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$;

and Tri-methyl-ethyl-methane, $C_2H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$.

The members of the first class are called *normal paraffins;* those of the second class, *iso-paraffins;* and those of the third class, *neo-paraffins.*

Only the members of the same class are strictly comparable with each other. Thus it has been found that the boiling-points of the normal hydrocarbons bear simple relations to each other, and that the same is true of the iso-paraffins; but, on comparing the boiling-points and other physical properties of normal paraffins with those of the iso- or neo-paraffins, no such simple relations are observed.

Regarding the names of the paraffins, the simplest nomenclature in use is that according to which the hydrocarbons are all regarded as derivatives of methane. Thus we get the name ethyl-methane for propane, $C\begin{cases} C_2H_5 \\ H \\ H \\ H \end{cases}$; tri-methyl-methane for isobutane, $C\begin{cases} CH_3 \\ CH_3 \\ CH_3 \\ H \end{cases}$; tetra-methyl-methane, $C\begin{cases} CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \end{cases}$, etc.

CHAPTER IX.

OXYGEN DERIVATIVES OF THE HIGHER MEMBERS OF THE PARAFFIN SERIES.

We are now to take up the derivatives of the higher members of the paraffin series, just as we took up the derivatives of methane and ethane. Not much need be said in regard to the halogen derivatives. A few of them will be mentioned in connection with the corresponding alcohols. The chief substances that will require attention are the alcohols and acids.

1. Alcohols.

Normal propyl alcohol, Propanol, $C_3H_7.OH$. — When sugar undergoes fermentation, a little propyl alcohol is always formed, and is contained in the "fusel oil." From this it can be separated by treating those portions which boil between 85° and 110° with phosphorus and bromine. The bromides of the alcohols present are thus formed (what is the reaction?), and these are separated by fractional distillation. The bromide corresponding to propyl alcohol is then converted into the alcohol (how can this be done?).

It is a colorless liquid with a pleasant odor. It boils at 97° (compare with the boiling-points of methyl and ethyl alcohol). It conducts itself almost exactly like the first two members of the series. By oxidation it is converted into an aldehyde, C_3H_6O, and an acid, $C_3H_6O_2$, which bear to it the same relations that acetic aldehyde and acetic acid bear to ethyl alcohol.

Secondary propyl or isopropyl alcohol, $C_3H_7.OH$. — The reasons for regarding the alcohols as hydroxyl derivatives

of the hydrocarbons have been given pretty fully. As the six hydrogen atoms of ethane are all of the same kind, but one ethyl alcohol appears to be possible and only one is known. But just as there are two butanes or methyl derivatives of propane, so there are two hydroxyl derivatives of propane; or, in other words, two propyl alcohols. The first is the one obtained from "fusel oil," the other is the one called secondary propyl alcohol. This has already been referred to under the head of Acetone (see p. 72), where it was stated that acetone is converted into secondary propyl alcohol by nascent hydrogen. We are, in fact, dependent upon this method for the preparation of the alcohol.

It is, like ordinary propyl alcohol, a colorless liquid. It boils at 81°. While all its reactions show that it is a hydroxide, under the influence of oxidizing agents it conducts itself quite differently from the alcohols thus far considered. It is converted first into acetone, C_3H_6O, which is isomeric with the aldehyde obtained from ordinary propyl alcohol; by further oxidation, it however does not yield an acid of the formula $C_3H_6O_2$, as we should expect it to, but breaks down, yielding two simpler acids; viz., formic acid, CH_2O_2, and acetic acid, $C_2H_4O_2$.

Secondary alcohols. — Secondary propyl alcohol is the simplest representative of a class of alcohols that are known as *secondary alcohols*. They are made by treating the ketones with nascent hydrogen, and are easily distinguished from other alcohols by their conduct towards oxidizing agents. They yield acetones containing the same number of carbon atoms, and then break down, yielding acids containing a smaller number of carbon atoms.

Is there anything in the structure of these secondary alcohols to suggest an explanation of their conduct? Secondary propyl alcohol is made from acetone by treating with nascent hydrogen. Acetone contains two methyl groups and carbonyl,

as represented by the formula $CH_3-CO-CH_3$. The simplest change that we can imagine as taking place in this compound under the influence of hydrogen is that represented in the following equation: —

$$CH_3-CO-CH_3 + H_2 = CH_3-CH.OH-CH_3.$$

The very close connection existing between acetone and secondary propyl alcohol, and the fact that there are two methyl groups in acetone, make it appear probable that there are also two methyl groups in secondary propyl alcohol, as represented in the above equation. On the other hand, the easy transformation of primary propyl alcohol into propionic acid, which can be shown to contain ethyl, shows that in the alcohol ethyl is present. Therefore, we may conclude that the difference between primary and secondary propyl alcohol is that the former is an ethyl derivative and the latter a di-methyl derivative of methyl alcohol, as represented by the formulas: —

$$C\begin{cases} H \\ H \\ H \\ OH \end{cases}$$

Methyl alcohol.

$$C\begin{cases} CH_2\cdot CH_3 \\ H \\ H \\ OH \end{cases}$$

Ethyl-methyl alcohol or ordinary propyl alcohol.

$$C\begin{cases} CH_3 \\ CH_3. \\ H \\ OH \end{cases}$$

Dimethyl-methyl alcohol or secondary propyl alcohol.

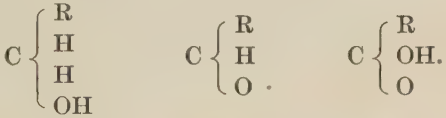
Primary propyl alcohol is *methyl alcohol in which one hydrogen is replaced by a radical*, while secondary propyl alcohol is *methyl alcohol in which two hydrogens are replaced by radicals*. An examination of all secondary alcohols known shows that the above statement can be made in regard to all of them. They must be regarded as derived from methyl alcohol by the replacement of two hydrogen atoms by radicals. The alcohols of the first class, like methyl, ethyl, and ordinary propyl alcohols, which are derived from methyl alcohol by the replacement of one hydrogen by a radical, are called *primary alcohols*. Another way of stating the difference between primary and

secondary alcohols is this: Primary alcohols contain the group CH_2OH; secondary alcohols contain the group CHOH. These statements necessarily follow from the first ones.

A primary alcohol, when oxidized, yields an aldehyde and an acid containing the same number of carbon atoms as the alcohol.

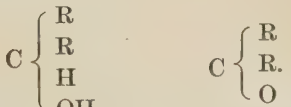
A secondary alcohol, when oxidized, yields an acetone, and then an acid or acids containing a smaller number of carbon atoms.

Recalling what was said regarding the nature of the changes involved in passing from an alcohol to the corresponding aldehyde and acid, it will be seen that the formation of the acid is impossible in the case of a secondary alcohol. In the case of a primary alcohol, we have:—



Alcohol. Aldehyde. Acid.

In the case of the secondary alcohol, we have:—



Secondary alcohol. Ketone.

Further introduction of oxygen cannot take place without a breaking down of the compound. It will be seen that the formulas used to express the structure of the compounds are remarkably in accordance with the facts.

Butyl alcohols, $C_4H_9.OH$. — Theoretically, there are two possible hydroxyl derivatives of each of the two butanes, making four butyl alcohols in all. They are all known. Two are primary alcohols.

1. **Normal butyl alcohol,** $CH_3.CH_2.CH_2.CH_2.OH$.

2. **Isobutyl alcohol,** $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CH_2OH$.

The third is a derivative of normal butane, and is a secondary alcohol.

3. **Secondary butyl alcohol,** $CH_3.CH_2.CH<\begin{matrix}OH\\CH_3\end{matrix}$. This alcohol is prepared by treating ethyl-methyl ketone with nascent hydrogen: —

$$CH_3.CH_2-CO-CH_3 + H_2 = CH_3.CH_2.CH<\begin{matrix}OH\\CH_3\end{matrix}.$$

(Compare this with the reaction for making secondary propyl alcohol.)

4. **Tertiary butyl alcohol,** $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$. The fourth butyl alcohol has properties which distinguish it from the primary and secondary alcohols. When oxidized it yields neither an aldehyde nor an acetone, but breaks down at once, yielding acids containing a smaller number of carbon atoms. Assuming that every primary alcohol contains the group CH_2OH, and that every secondary alcohol contains the group CHOH, it follows that the two primary butyl alcohols and secondary butyl alcohol must have the formulas above assigned to them; and it follows further, that the fourth butyl alcohol must have the formula $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$, as this represents the only other arrangement of the constituents possible, according to our theory. This formula represents a condition which does not exist in either the primary or secondary alcohols. It is methyl alcohol in which all the hydrogen atoms, except that in the hydroxyl, are replaced by methyl groups, and it contains the group C — (OH). Such an alcohol is known as a *tertiary alcohol*, and the one under consideration

is called *tertiary butyl alcohol.* It is the simplest derivative of a class of which but few members are known.

Tertiary butyl alcohol is made by treating acetyl chloride, $CH_3.COCl$, with zinc methyl, $Zn(CH_3)_2$. These two substances unite, forming a crystallized compound; and, when this is treated with water, it breaks up, yielding acetone: —

$$CH_3.C\begin{cases} O \\ Cl \end{cases} + Zn(CH_3)_2 = CH_3.C\begin{cases} CH_3 \\ O.ZnCH_3 \\ Cl \end{cases};$$

$$CH_3.C\begin{cases} CH_3 \\ OZnCH_3 \\ Cl \end{cases} + 2\,H_2O = CH_3.CO.CH_3 + Zn(OH)_2 + HCl + CH_4.$$

If, however, a second molecule of zinc methyl reacts upon the product first formed, the change represented by the following equation takes place: —

$$CH_3.C\begin{cases} CH_3 \\ OZnCH_3 \\ Cl \end{cases} + Zn(CH_3)_2 = CH_3.C\begin{cases} CH_3 \\ OZnCH_3 + Zn < \begin{matrix} Cl \\ CH_3 \end{matrix} \\ CH_3 \end{cases}.$$

By treating the product with water, tertiary butyl alcohol is formed: —

$$CH_3.C\begin{cases} CH_3 \\ OZnCH_3 \\ CH_3 \end{cases} + 2\,H_2O = CH_3.C\begin{cases} CH_3 \\ OH \\ CH_3 \end{cases} + Zn(OH)_2 + CH_4.$$

By taking other acid chlorides, and the zinc compounds of other radicals, other tertiary alcohols may be obtained.

Characteristics of the three Classes of Alcohols. To recapitulate briefly, the hydroxyl derivatives of the hydrocarbons can be divided into three classes, according to their conduct towards oxidizing agents.

To what was said above regarding the conduct of primary and secondary alcohols we can now add: Tertiary alcohols yield neither aldehydes nor acetones containing the same number of carbon atoms, but generally break down, yielding simpler acids.

The general formulas representing the three classes of alcohols are: —

$$C\begin{cases} R \\ H \\ H \\ OH \end{cases} \qquad C\begin{cases} R \\ R \\ H \\ OH \end{cases} \quad \text{and} \quad C\begin{cases} R \\ R \\ R \\ OH \end{cases}$$

Primary. Secondary. Tertiary.

Pentyl alcohols, $C_5H_{11}.OH$. — Eight of these are possible, and seven are known. Only the two *amyl alcohols* need be taken up here.

Inactive amyl alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH - CH_2 - CH_2OH$. — This alcohol, together with at least one other of the same composition, forms the chief part of "fusel oil." By fractional distillation of this, ordinary amyl alcohol is obtained, as a colorless liquid, having a penetrating odor, and boiling at 131° to 132°. This can be separated by other methods into two isomeric alcohols, one of which is *inactive* amyl alcohol and the other *active* amyl alcohol. The names refer to the behavior of the substances towards polarized light, the former having no action upon it, the latter turning the plane of polarization to the left.

When oxidized, inactive amyl alcohol yields an acid containing the same number of carbon atoms, and is, therefore, a primary alcohol. The acid has been made by simple reactions which show that it must be represented by the formula $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH.CH_2.CO_2H$. Therefore, the alcohol has the structure represented by the formula $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH.CH_2.CH_2OH$.

Active amyl alcohol, $CH_3.CH_2.CH < \begin{matrix} CH_3 \\ CH_2OH \end{matrix}$. — This, as has been stated, is obtained, together with the inactive alcohol, from fusel oil. It is a primary alcohol as represented.

A list of some of the more important remaining members of the series is given below. In naming the alcohols, it is best to refer them to methyl alcohol, just as the hydrocarbons are referred to marsh gas. Calling methyl alcohol *carbinol*, we get such names as methyl-carbinol, di-ethyl-carbinol, etc., which convey at once an accurate idea

concerning the structure of the substances. A few illustrations will suffice. Take the alcohols considered above: —

Ethyl alcohol is *methyl-carbinol*, $C\begin{cases}CH_3\\H\\H\\OH\end{cases}$;

Primary propyl alcohol is *ethyl-carbinol*, $C\begin{cases}CH_2CH_3\\H\\H\\OH\end{cases}$;

Secondary propyl alcohol is *di-methyl-carbinol*, $C\begin{cases}CH_3\\CH_3\\H\\OH\end{cases}$;

Tertiary butyl alcohol is *tri-methyl-carbinol*, $C\begin{cases}CH_3\\CH_3\\CH_3\\OH\end{cases}$;

Inactive amyl alcohol is *isobutyl-carbinol*, $C\begin{cases}CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}\\H\\H\\OH,\ \text{etc., etc.,}\end{cases}$

a name given to it on account of the presence in it of the isobutyl group $CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}$.

The following table will give an imperfect idea of the extent to which the series of alcohols derived from the paraffins is developed. There are thirteen hexyl alcohols and thirteen heptyl alcohols known. Of most of the higher members but one variety is known. They are not important, except in so far as they indicate the possibility of the discovery of other alcohols.

ALCOHOLS OF THE METHYL ALCOHOL SERIES.

SERIES $C_nH_{2n+1}.OH$.

Methyl alcohol	$CH_3.OH$.
Ethyl "	$C_2H_5.OH$.
Propyl "	$C_3H_7.OH$.
Butyl "	$C_4H_9.OH$.
Pentyl "	$C_5H_{11}.OH$.
Hexyl "	$C_6H_{13}.OH$.
Heptyl "	$C_7H_{15}.OH$.
Octyl "	$C_8H_{17}.OH$.
Nonyl "	$C_9H_{19}.OH$.
Cetyl "	$C_{16}H_{33}.OH$.
Ceryl "	$C_{27}H_{55}.OH$.
Myricyl "	$C_{30}H_{61}.OH$.

2. ALDEHYDES.

In general, it follows from what has been said concerning the properties of primary alcohols, that there should be an aldehyde corresponding to every primary alcohol. Many of these have been prepared. They resemble ordinary acetic aldehyde so closely that it is unnecessary to take them up individually. If we know the structure of the alcohol from which an aldehyde is formed by oxidation, we also know the structure of the aldehyde.

Besides the one method for the preparation of aldehydes which has been mentioned, viz., the oxidation of primary alcohols, there is one other which should be specially noticed. It consists in distilling a mixture of a formate and a salt of some other acid. Thus, when a mixture of an acetate and a formate is distilled, acetic aldehyde is formed as represented by the equation: —

$$\begin{matrix} CH_3.COOM \\ H.COOM \end{matrix} = \underset{\text{Aldehyde.}}{CH_3.COH} + M_2CO_3.$$

This method has been used to a considerable extent in making the higher members of the series.

Experiment 32. Mix about equal weights of dry calcium formate and dry calcium acetate. Distil from a small flask. Collect some of the distillate in water, and determine whether aldehyde is formed.

3. Acids.

Formic and acetic acids are the first two members of an homologous series of similar acids, generally called the *fatty acids* because several of them occur in large quantities in the natural fats. The names and formulas of some of the principal members are given in the following table. The reasons for representing the acids as compounds containing the carboxyl group, CO_2H, have been given, and need not here be restated: —

FATTY ACIDS.

Series $C_nH_{2n+1}.CO_2H$, or $C_nH_{2n}O_2$.

Formic acid	$H.CO_2H$.
Acetic "	$CH_3.CO_2H$.
Propionic "	$C_2H_5.CO_2H$.
Butyric "	$C_3H_7.CO_2H$.
Valeric "	$C_4H_9.CO_2H$.
Caproic or Hexoic acids	$C_5H_{11}.CO_2H$.
Œnanthylic or Heptoic acids	$C_6H_{13}.CO_2H$.
Caprylic or Octoic acids	$C_7H_{15}.CO_2H$.
Pelargonic or Nonoic acids	$C_8H_{17}.CO_2H$.
Capric acid	$C_9H_{19}.CO_2H$.

Lauric	acid	$C_{11}H_{23}.CO_2H.$
Myristic	"	$C_{13}H_{27}.CO_2H.$
Palmitic	"	$C_{15}H_{31}.CO_2H.$
Margaric	"	$C_{16}H_{33}.CO_2H.$
Stearic	"	$C_{17}H_{35}.CO_2H.$
Arachidic	"	$C_{19}H_{39}.CO_2H.$
Behenic	"	$C_{21}H_{43}.CO_2H.$
Hyenic	"	$C_{24}H_{49}.CO_2H.$
Cerotic	"	$C_{26}H_{53}.CO_2H.$
Melissic	"	$C_{29}H_{59}.CO_2H.$

Although, as will be seen, a large number of fatty acids are known, most of them included in the list are at present merely curiosities, and need not be specially studied. Not more than six in addition to formic and acetic acids will require attention.

Propionic acid, Propanic acid, $C_3H_6O_2(C_2H_5.CO_2H)$. — Propionic acid is formed in small quantity (1) by the distillation of wood; (2) by the fermentation of various organic bodies, particularly calcium lactate and tartrate; (3) by treating ethyl cyanide (propio-nitrile) with caustic potash: —

$$C_2H_5.CN + KOH + H_2O = C_2H_5.CO_2K + NH_3;$$

and (4) by oxidizing normal propyl alcohol. This last method is used on the large scale.

Other methods for preparing it are the following: —

(1) By reducing lactic acid with hydriodic acid. (This will be explained under the head of Lactic Acid, which see.)

(2) By the action of carbon dioxide upon sodium ethyl: —

$$CO_2 + NaC_2H_5 = C_2H_5.CO_2Na.$$

It is a colorless liquid with a penetrating odor somewhat resembling that of acetic acid. It boils at 141°. (Compare with boiling-points of formic and acetic acids.)

It yields a large number of derivatives corresponding to those obtained from acetic acid.

NOTE FOR STUDENT. — What is propionyl chloride? and how can it be prepared? It is analogous to acetyl chloride.

The simple substitution-products of propionic acid present an interesting and instructive case of isomerism. There are two chlor-propionic acids, two brom-propionic acids, etc. Those products which are obtained by direct treatment of propionic acid with substituting agents are called α-products, and the isomeric substances β-products. Thus we have *α-chlor-propionic* and *α-brom-propionic acid*, made by treating propionic acid with chlorine and bromine; and *β-chlor-propionic acid* and *β-brom-propionic acid*, made by indirect methods. The difference between these two series of derivatives is due to different relations between the constituents. The usual method of representation indicates the possibility of the existence of two isomeric chlor-propionic acids, and of similar mono-substitution products of propionic acid. The acid is represented thus: —

$$CH_3.CH_2.CO_2H.$$

Now, if chlorine should enter into the compound, as represented by the formula $CH_2Cl.CH_2.CO_2H$, (1) we should have one of the chlor-propionic acids; while, if it should enter as indicated in the formula $CH_3.CHCl.CO_2H$, (2) we should have the isomeric product. We have thus two chlor-propionic acids actually known, and our theory gives us two formulas. How can we tell which of the formulas represents α-chlor-propionic acid, and which the β-acid? Only by carefully studying all the reactions and methods of formation of both compounds. The best evidence is furnished by a study of the lactic acids, which will be shown to be mono-substitution products of propionic acid. α-Chlor-propionic acid can be transformed into a lactic acid, the structure of which is represented by the formula $CH_3.CH(OH).CO_2H$, and by replacing the hydroxyl of this

lactic acid by chlorine, α-chlor-propionic acid is formed. It therefore follows that formula (2) above given is that of α-chlor-propionic acid, and formula (1) that of β-chlor-propionic acid. Further, any mono-substitution product of propionic acid that can be made directly from α-chlor-propionic acid, or converted directly into this acid, is an α-product, and has the general formula

$$CH_3.CHX.CO_2H;$$

and, similarly, the β-products have the general formula

$$CH_2X.CH_2.CO_2H,$$

in which X represents any univalent atom or group.

Butyric acids, Butanic acids, $C_4H_8O_2(C_3H_7.CO_2H)$.

Normal butyric acid, $CH_3.CH_2.CH_2.CO_2H$. When butter is boiled with caustic potash, the potassium salts of butyric acid and of some of the higher members of the series are found in the solution at the end of the operation. Butter, like other fats, belongs to the class of compounds known as ethereal salts; and these, as we have seen, when boiled with the alkalies, are decomposed, yielding alcohol and alkali salts of acids (saponification). In the case of butter and of nearly all other fats, the alcohol formed is *glycerol.* Butyric acid occurs also in many other fats besides butter.

It is most readily made by fermentation of sugar by what is known as the *butyric acid ferment.* This ferment probably is contained in putrid cheese. Hence, to make the acid, sugar and tartaric acid are dissolved in water, and, after a time, certain quantities of putrid cheese and sour milk are added, and also some powdered chalk. At first the sugar is converted into glucose: —

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = 2\,\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

The glucose breaks up, yielding lactic acid, $C_3H_6O_3$: —

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2\,\underset{\text{Lactic acid.}}{C_3H_6O_3}.$$

And, finally, the lactic acid is converted into butyric acid: —

$$2\,C_3H_6O_3 = C_4H_8O_2 + 2\,CO_2 + 4\,H.$$

Other methods for the preparation of butyric acid are: —

(1) By oxidation of normal butyl alcohol; and

(2) By treating normal propyl cyanide, $CH_3.CH_2.CH_2CN$, with caustic potash.

The acid is a liquid having an acid, rancid odor, like that of rancid butter. It boils at 162°. (Compare with the preceding acids.) Like the lower members of the series it mixes with water in all proportions.

Ethyl butyrate, $C_3H_7.CO_2C_2H_5$, has a pleasant odor resembling that of pineapples. It is used under the name of *essence of pineapples*.

Isobutyric acid, Methyl-propanic acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CO_2H$. — From the two propyl alcohols the two chlorides, propyl chloride, $CH_3.CH_2.CH_2Cl$, and isopropyl chloride, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CHCl$, can be made, and from these the corresponding cyanides, —

Propyl cyanide . . . . . $CH_3.CH_2.CH_2CN$,

and Isopropyl cyanide . . . . $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CHCN$.

By boiling with caustic potash, the former is converted into normal butyric acid, as stated above; while the latter yields isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CO_2H$. This acid can be prepared also by oxidizing isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.CH_2OH$. It is found in nature in the carob bean.

Isobutyric acid is a liquid which boils at 154°. Its odor is less unpleasant than that of the normal acid.

Valeric acids, $C_5H_{10}O_2(C_4H_9.CO_2H)$. — Four carboxyl derivatives of the butanes are possible. Four acids of the formula $C_5H_{10}O_2$ are known.

Inactive or ordinary valeric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CO_2H$. — This acid is made by oxidizing inactive amyl alcohol. It can also be made (and this reaction reveals the structure of the acid) by starting with isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$, converting this first into the chloride and then into the cyanide, and, finally, transforming the cyanide, which is $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2CN$, into the acid. It occurs in valerian root, whence its name. It is an unpleasant smelling liquid, boiling at 174°. It requires thirty parts of water for solution.

Amyl valerate, $C_4H_9.CO_2C_5H_{11}$, has the odor of apples, and is used under the name of *essence of apples*.

Active valeric acid, $\begin{matrix}CH_3\\CO_2H\end{matrix}>CH.CH_2.CH_3$. — This acid is prepared by oxidation of active amyl alcohol. Although the alcohol turns the plane of polarization to the left, the acid turns it to the right. The alcohol is said to be *lævo-rotatory*, and the acid *dextro-rotatory*.

The higher acids of the series are, for the most part, found in various fats. They are difficultly soluble in water. The highest members are solids. The two best known, because occurring in largest quantity, are *palmitic* and *stearic acids*. These are contained in combination with the alcohol, glycerol, in all the common fats. The fats will be treated under the head of Glycerol.

Palmitic acid, $C_{15}H_{31}.CO_2H$, can be made by saponifying many fats, as palm oil, olive oil, and bayberry tallow. The last-named fat consists of about one-fifth part of palmitin, four-fifths being free palmitic acid and a little lauric acid and laurin. It crystallizes in needles which melt at 62.6°.

Stearic acid, $C_{17}H_{35}.CO_2H$, is the acid contained in that particular fat known as *stearin*. The so-called "stearin can-

dles" consist of stearic acid mixed with palmitic acid and a little paraffin, and from them stearic acid can be separated in pure form by long-continued fractional crystallization from ether and alcohol.

It crystallizes from alcohol in needles or laminæ which melt at 69.3°.

Soaps. — In speaking of the decompositions of ethereal salts by boiling with alkalies, it was stated that this process is called saponification because it is best exemplified in the manufacture of soaps from fats. The fats are themselves rather complicated ethereal salts. When they are boiled with an alkali, as caustic soda, the alcohol is liberated, and the alkali salts of the acids are formed. *These salts are the soaps.* They are in solution after the process of saponification is completed, and can be separated by adding a solution of common salt, in which they are insoluble.

Experiment 33. In an iron pot boil about 25g of lard with a solution of caustic soda for two hours. After cooling, add a strong solution of sodium chloride. The soap will separate and rise to the top of the solution, where it will finally solidify. Dissolve some of the soap thus obtained in water, and filter. Add hydrochloric acid, when the free fatty acids, mainly palmitic and stearic acids, will separate as solids, which will rise to the top. The hydrochloric acid simply decomposes the sodium palmitate and stearate, giving free palmitic and stearic acids and sodium chloride: —

$$\underset{\text{Sodium Palmitate.}}{C_{15}H_{31}.CO_2Na} + HCl = \underset{\text{Palmitic Acid.}}{C_{15}H_{31}.CO_2H} + NaCl,$$

and

$$\underset{\text{Sodium Stearate.}}{C_{17}H_{35}.CO_2Na} + HCl = \underset{\text{Stearic Acid.}}{C_{17}H_{35}.CO_2H} + NaCl.$$

The remaining derivatives of the higher members of the paraffin series include the ethers, ketones, ethereal salts, mercaptans, sulphur ethers, sulphonic acids, cyanides and isocyanides, cyanates and isocyanates, sulpho-cyanates and

iso-sulpho-cyanates, substituted ammonias and analogous compounds, metal derivatives, and nitro-derivatives.

A great many substances belonging to these classes, and containing residues of the higher hydrocarbons, have been prepared and studied; but, in the main, they so closely resemble the simpler substances which have already been described that we should gain nothing by taking them up here individually. The student, however, is earnestly advised to apply the principles discussed in the first part of the book to a few other cases. Thus, let him take propane and butane, and, not only write the formulas of the derivatives which can be obtained from them, but, above all, write the equations representing the action involved in their preparation, and the transformations of which they are capable.

POLYACID ALCOHOLS AND POLYBASIC ACIDS.

1. Di-acid Alcohols.

The alcohols thus far treated of are of the simplest kind. They correspond to the simplest metallic hydroxides, as potassium hydroxide, KOH. Just as these simplest metallic hydroxides are called *mon-acid bases*, so the simplest alcohols are called *mon-acid alcohols*,[1] expressions which are suggested by the term *mono-basic acid*. But, as is well known, there are metallic hydroxides, like calcium hydroxide, $Ca(OH)_2$, barium hydroxide, $Ba(OH)_2$, etc., which contain two hydroxyls, and are hence known as *di-acid bases;* and so, too, there are *di-acid alcohols* which bear to the mon-acid alcohols the same relation that the di-acid bases bear to the mon-acid bases. Only one alcohol of this kind, derived from the paraffin hydrocarbons, is well known.

Ethylene alcohol or glycol, Ethandiol, $C_2H_6O_2[C_2H_4(OH)_2]$. — Glycol is made by starting with ethylene, a hydro-

[1] The expression *monatomic* alcohols is used by some writers, but, as it is confusing, it is gradually giving way to the more rational expression above used.

carbon of the formula C_2H_4. When this is brought together with bromine, the two unite directly, forming *ethylene bromide*, $C_2H_4Br_2$. By replacing the two bromine atoms by hydroxyl, ethylene alcohol or glycol is formed.

It is a colorless, inodorous, somewhat oily liquid, which boils at 197.5°. It has a sweetish taste, and is hence called *glycol* (from γλυκύς, *sweet*). Hence, further, the other alcohols of this series are also called *glycols*.

The derivatives of ethylene alcohol are not as numerous as those of the better known members of the methyl alcohol series, but those which are known are of the same general character. The reactions of the alcohol are the same as those of the mon-acid alcohols, but it presents more possibilities. In most cases in which a mon-acid alcohol yields one derivative, ethylene alcohol yields two. Thus, with sodium, the two compounds, *sodium glycol*, $C_2H_4 < \begin{matrix} ONa \\ OH \end{matrix}$, and *di-sodium glycol*, $C_2H_4 < \begin{matrix} ONa \\ ONa \end{matrix}$, can be formed; from these, by treating with ethyl iodide, the two ethers, *ethyl-glycol ether*, $C_2H_4 < \begin{matrix} OC_2H_5 \\ OH \end{matrix}$, and *di-ethyl-glycol ether*, $C_2H_4 < \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$, are made. By treatment with hydrochloric acid, the chloride, $C_2H_4 < \begin{matrix} Cl \\ OH \end{matrix}$, known as *ethylene chlorhydrine* is formed; and this, by treatment with phosphorus trichloride, can be converted into ethylene chloride, $C_2H_4Cl_2$, etc.

Its conduct towards acids is like that of a di-acid base. It forms *neutral* and *alcoholic salts*, of which the acetates may serve as examples. Thus we have the

$$\textit{Mono-acetate},\ C_2H_4 < \begin{matrix} O.C_2H_3O \\ OH \end{matrix},$$

and the

$$\textit{Di-acetate},\quad C_2H_4 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix};$$

the former still containing alcoholic hydroxyl and corresponding to a basic salt; the latter being a neutral compound.

The formation of the diacetate is a step in one of the methods of preparing ethylene alcohol. This method consists in treating ethylene bromide with potassium acetate in alcoholic solution, separating the acetates of ethylene thus formed, and decomposing these by means of barium hydroxide. The reactions involved are represented by the following equations: —

$$C_2H_4{<}\begin{matrix}Br\\Br\end{matrix} + \begin{matrix}KO.C_2H_3O\\KO.C_2H_3O\end{matrix} = C_2H_4{<}\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix} + 2\,KBr;$$

and $$C_2H_4{<}\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix} + Ba{<}\begin{matrix}OH\\OH\end{matrix} = C_2H_4{<}\begin{matrix}OH\\OH\end{matrix} + Ba(C_2H_3O_2)_2.$$

The alcohol can also be made by treating ethylene bromide with potassium carbonate: —

$$C_2H_4{<}\begin{matrix}Br\\Br\end{matrix} + \begin{matrix}KO\\KO\end{matrix}{>}CO + H_2O = C_2H_4{<}\begin{matrix}OH\\OH\end{matrix} + 2\,KBr + CO_2;$$

and by treating ethylene bromide with silver oxide: —

$$C_2H_4{<}\begin{matrix}Br\\Br\end{matrix} + Ag_2O + H_2O = C_2H_4{<}\begin{matrix}OH\\OH\end{matrix} + 2\,AgBr.$$

These methods of formation show clearly what ethylene alcohol is.

When acetyl chloride acts upon the alcohol at ordinary temperature, the product has the formula $C_2H_4{<}\begin{matrix}OC_2H_3O\\Cl\end{matrix}$. This is also formed by the action of hydrochloric acid gas on the diacetate. It seems probable, therefore, that the action of acetyl chloride is to be represented by two equations; thus: —

$$C_2H_4{<}\begin{matrix}OH\\OH\end{matrix} + 2\,C_2H_3OCl = C_2H_4{<}\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix} + 2\,HCl;$$

and $$C_2H_4{<}\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix} + HCl = C_2H_4{<}\begin{matrix}OC_2H_3O\\Cl\end{matrix} + C_2H_4O_2.$$

There are two ways in which the structure of a compound of the formula $C_2H_4(OH)_2$ can be represented. They are, — (1) $\begin{matrix}CH_2(OH)\\|\\CH_2(OH)\end{matrix}$, in which each hydroxyl is represented in combination with a different carbon atom; and (2) $\begin{matrix}CH(OH)_2\\|\\CH_3\end{matrix}$, in which both hydroxyls are represented in combination with the same

carbon atom. The question at once suggests itself, to which of these formulas does ethylene alcohol correspond? To answer this question, we must recall what was said regarding the two dichlor-ethanes, known as *ethylene chloride* and *ethylidene chloride*. The former of these corresponds to the formula $CH_2Cl.CH_2Cl$, while the latter, which is formed from aldehyde by replacing the carbonyl oxygen by two chlorine atoms, is represented by the formula $CHCl_2.CH_3$. When the chlorine atoms of ethylene chloride are replaced by hydroxyl, ethylene alcohol is produced. Hence, the alcohol has the formula $\begin{matrix}CH_2(OH)\\ |\\ CH_2(OH)\end{matrix}$, or each of the hydroxyls is in combination with a different carbon atom.

All attempts to make the isomeric di-acid alcohol corresponding to ethylidene chloride, and having both hydroxyls in combination with the same carbon atom, as represented in the formula $\begin{matrix}CH(OH_2)\\ |\\ CH_3\end{matrix}$, have failed. Instead of getting ethylidene alcohol, aldehyde is generally obtained. Aldehyde is ethylidene alcohol minus water: —

$$\begin{matrix}CH(OH)_2\\ |\\ CH_3\end{matrix} = \begin{matrix}CHO\\ |\\ CH_3\end{matrix} + H_2O.$$

It is believed that one carbon atom cannot, under ordinary circumstances, hold in combination more than one hydroxyl group. If this is true, then ethylidene alcohol cannot be prepared any more than the hypothetical carbonic acid, $CO<\begin{matrix}OH\\ OH\end{matrix}$, can be. So, too, the simplest di-acid alcohol conceivable, viz., methylene alcohol, $CH_2(OH)_2$, cannot exist, but would break up, if formed at all, into water and formic aldehyde: —

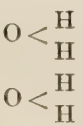
$$CH_2(OH)_2 = H_2O + H.CHO.$$

(See discussion regarding the transformation of alcohol into aldehyde, pp. 64–66.)

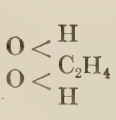
Ethyl alcohol, as was pointed out, may be regarded either as ethane in which one hydrogen is replaced by hydroxyl, or as water in which one hydrogen is replaced by the radical C_2H_5, or ethyl. Ethyl, like all the radicals contained in the mon-acid alcohols, is *univalent*. It is ethane less one atom of hydrogen, just as methyl is methane less one atom of hydrogen. Each has the power of uniting with one atom of hydrogen, or another univalent element, or of taking the place of one atom of hydrogen.

If we take away two atoms of hydrogen from methane and ethane, we have left the residues or radicals CH_2 and C_2H_4. These can unite with two atoms of hydrogen, or take the place of two atoms of hydrogen, and they are hence called *bivalent radicals*.

Just as ethylene alcohol may be regarded as ethane in which two hydrogen atoms are replaced by hydroxyls, so it may be regarded as water in which the bivalent radical ethylene replaces two hydrogens belonging to two different molecules of water: —



Two molecules water.



Ethylene alcohol.

The higher members of the series of di-acid alcohols will not be considered here.

2. Dibasic Acids.

Just as there are di-acid alcohols derived from the paraffins, so there are dibasic acids which may also be regarded as derivatives of the paraffins. We have seen that the simplest acids, the monobasic fatty acids, are closely related to formic and carbonic acids; that they may be regarded as derived from the latter by replacement of a hydroxyl by a radical, or as derived

from the paraffins by the introduction of the group carboxyl, CO_2H. The conditions existing in this group are essential to the acid properties. If two carboxyls are introduced into marsh gas, a substance of the formula $CH_2(CO_2H)_2$ is formed, and this is a dibasic acid. It contains two acid hydrogens, and is capable of forming two series of salts, the acid and neutral salts, like other dibasic acids. It may be regarded also as derived from two molecules of carbonic acid by the replacement of two hydroxyls by the bivalent radical CH_2: —

$$CO<\begin{matrix}OH\\OH\end{matrix} \qquad CO<\begin{matrix}OH\\OH\end{matrix}$$

Two molecules carbonic acid.

$$CO<\begin{matrix}OH\\CH_2\end{matrix} \qquad CO<\begin{matrix}\\OH\end{matrix}$$

Dibasic acid.

The general methods of preparation available for the building up of the series of dibasic acids are modifications of those used in making the monobasic acids. They are: —

1. *Oxidation of di-acid primary alcohols.* Just as a mon-acid primary alcohol, $R.CH_2OH$, yields by oxidation a monobasic acid, so a di-acid primary alcohol, $R''(CH_2OH)_2$, yields a dibasic acid, $R''(CO_2H)_2$.

2. *Treatment of the dicyanides,* $R''(CN)_2$, *with caustic alkalies.*

3. *Oxidation of the hydroxy-acids or alcohol acids.* These are compounds which are at the same time alcohol and acid; as, for example, hydroxy-acetic acid, which is acetic acid in which one of the hydrogen atoms of the hydrocarbon residue, methyl, has been replaced by hydroxyl, as represented in the formula $\begin{matrix}CH_2OH\\|\\CO_2H\end{matrix}$. When this is oxidized, the alcoholic portion, CH_2OH, is converted into carboxyl, and a dibasic acid is formed.

4. From the cyanogen derivatives of the monobasic acids, such as cyan-acetic acid, $CH_2<\begin{matrix}CN\\CO_2H\end{matrix}$, by the transformation of the cyanogen group into carboxyl.

DIBASIC ACIDS, $C_nH_{2n-2}O_4$.

Oxalic	acid	$(CO_2H)_2$.
Malonic	"	$CH_2(CO_2H)_2$.
Succinic	"	$C_2H_4(CO_2H)_2$.
Pyrotartaric	"	$C_3H_6(CO_2H)_2$.
Adipic	"	$C_4H_8(CO_2H)_2$.
Pimelic	"	$C_5H_{10}(CO_2H)_2$.
Suberic	"	$C_6H_{12}(CO_2H)_2$.
Azelaic	"	$C_7H_{14}(CO_2H)_2$.
Sebacic	"	$C_8H_{16}(CO_2H)_2$.
Brassylic	"	$C_9H_{18}(CO_2H)_2$.
Roccellic	"	$C_{15}H_{30}(CO_2H)_2$.

Of the many acids included in this list only four or five can be said to be well known. We may confine our attention to the first four members.

Oxalic acid, $C_2H_2O_4[(CO_2H)_2]$. — In one sense, according to the accepted definition, oxalic acid is not a member of the series with which we are dealing, as it is not derived from a hydrocarbon by replacement of hydrogen by carboxyl; nor is it derived from two molecules of carbonic acid by replacement of two hydroxyls by a bivalent radical. Still it is in other respects so closely allied to the members of the series, and has so many things in common with the other members, that it would be a mere act of pedantry to consider it in any other connection.

Oxalic acid occurs very widely distributed in Nature; as in certain plants of the *oxalis* varieties, in the form of the acid potassium salt; as calcium salt in many plants; in urinary calculi; and as the ammonium salt in guano.

It is formed by the action of nitric acid upon many organic

substances, particularly the different varieties of sugar and the so-called carbohydrates, such as starch, cellulose, etc.

Experiment 34. In a good-sized flask pour half a litre of ordinary concentrated nitric acid (of specific gravity 1.245) upon 50g of sugar. Heat gently until the reaction begins. Then withdraw the flame, when the oxidation will proceed with some violence, and accompanied by a copious evolution of red fumes. When the action has ceased, evaporate the liquid to one-sixth the original volume, and let it cool, when oxalic acid will crystallize out. Recrystallize from water the acid thus obtained, and with the pure substance perform such experiments as will exhibit its properties. For example, (1) Heat a specimen at 100°, and notice loss of water; (2) Heat some in a small flask with sulphuric acid, and prove that both oxides of carbon are formed.

On the large scale, oxalic acid is made by heating wood shavings or saw-dust with caustic potash and caustic soda to 240° to 250°. The mass is extracted with water, and the solution evaporated to crystallization, when sodium oxalate is deposited.

Other methods, which are interesting from a purely scientific point of view, are the following: —

1. The spontaneous transformation of an aqueous solution of cyanogen: —

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4\,H_2O = \begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} + 2\,NH_3;$$

or, really,

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4\,H_2O = \begin{matrix} CO_2(NH_4) \\ | \\ CO_2(NH_4) \end{matrix}.$$

2. Treatment of carbon dioxide with sodium: —

$$2\,CO_2 + 2\,Na = C_2O_4Na_2.$$

3. Heating sodium formate: —

$$2\,H.CO_2Na = C_2O_4Na_2 + 2\,H.$$

Oxalic acid crystallizes from water in monoclinic prisms con-

taining two molecules of water ($C_2H_2O_4 + 2\,H_2O$). It loses this water at 100°. It sublimes without decomposition at 150° to 160°, but, if heated higher, it breaks up into carbon monoxide, carbon dioxide, and formic acid: —

$$2\,C_2H_2O_4 = 2\,CO_2 + CO + HCO_2H + H_2O.$$

Sulphuric acid decomposes it into carbon monoxide, carbon dioxide, and water. Heated with glycerol to 100°, carbon dioxide and formic acid are formed (see Formic Acid): —

$$C_2H_2O_4 = CO_2 + H.CO_2H.$$

It is an excellent reducing agent, and is used as a standardizer in preparing solutions of potassium permanganate.

Experiment 35. Try the action of a solution of potassium permanganate on a solution of oxalic acid. Why is it best to have the solution of the permanganate acid?

Oxalic acid is an active poison. It is used in calico printing.

Salts of oxalic acid. Like all dibasic acids, oxalic acid forms acid and neutral salts with metals. All the salts are insoluble except those containing the alkalies. Among those most common are the *acid potassium salt*, C_2O_4HK, which is found in the sorrels or plants of the *oxalis* variety; the *ammonium salt*, $C_2O_4(NH_4)_2$, of which some urinary calculi are formed; and calcium oxalate, C_2O_4Ca, which, being insoluble in water and acetic acid, is used as a means of detecting calcium in the presence of magnesium, and of estimating calcium and oxalic acid.

Malonic acid, $C_3H_4O_4[= CH_2(CO_2H)_2]$. — This acid was first made by oxidation of malic acid (which see), and is hence called *malonic acid*. It can best be made by starting with acetic acid. The necessary steps are: (1) making chlor-acetic acid; (2) transforming chlor-acetic acid into cyan-acetic acid; (3) heating cyan-acetic acid with an alkali.

NOTE FOR STUDENT. — Write the equations representing the three steps mentioned.

It is a solid which crystallizes in laminæ. It breaks up at a temperature above 132°, which is its melting-point, into carbon dioxide and acetic acid: —

$$CH_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = CH_3.CO_2H + CO_2.$$

NOTE FOR STUDENT. — What simple method for the preparation of marsh gas and other paraffins is this reaction analogous to?

Succinic acids, $C_4H_6O_4$ [$= C_2H_4(CO_2H)_2$]. — Regarding these acids as derived from ethane by substituting two carboxyls for two hydrogens, it is clear that there may be two, one corresponding to ethylene chloride and another corresponding to ethylidene chloride. Two are actually known. One is the well-known succinic acid; the other is called *isosuccinic acid.*

Succinic acid, Ethylene succinic acid, $\begin{matrix} CH_2.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$. — This acid occurs in amber (hence its name, from Lat. *succinum*, amber); in some varieties of lignite; in many plants; and in the animal organism, as in the urine of the horse, goat, and rabbit.

It is formed under many circumstances, especially by oxidation of fats with nitric acid, by fermentation of calcium malate, and, in small quantity, in the alcoholic fermentation of sugar. Among the methods for its preparation are: —

1. Treatment of ethylene cyanide, $\begin{matrix} CH_2.CN \\ | \\ CH_2.CN \end{matrix}$, with a caustic alkali: —

$$\begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} + 2\,KOH + 2\,H_2O = \begin{matrix} CH_2.CO_2K \\ | \\ CH_2.CO_2K \end{matrix} + 2\,NH_3.$$

2. Similarly, by treatment of β-cyan-propionic acid with an alkali. (What is β-cyan-propionic acid?)

3. Reduction of tartaric and malic acids by means of

hydriodic acid. These well-known acids will be shown to be closely related to succinic acid, and the reaction here mentioned will be explained. The methods actually used in the preparation of succinic acid are: (1) the distillation of amber, and (2) the fermentation of calcium malate.

The acid crystallizes in monoclinic prisms, which melt at 185° (try it). It boils at 235°, at the same time giving off water, and being converted into the *anhydride*: —

$$C_2H_4 < \begin{matrix} COOH \\ COOH \end{matrix} = C_2H_4 < \begin{matrix} CO \\ CO \end{matrix} > O + H_2O.$$

Succinic anhydride is a solid substance that crystallizes well from chloroform. It is converted into succinic acid by boiling with water. When boiled with alcohols it yields the corresponding ester acids. For example, with ordinary alcohol monoethyl succinate is formed.

$$C_2H_4 < \begin{matrix} CO \\ CO \end{matrix} > O + C_2H_5OH = C_2H_4 < \begin{matrix} COOC_2H_5 \\ COOH \end{matrix}.$$

Among the salts *basic ferric succinate*, $C_4H_4O_4.Fe(OH)$, is of special interest, as it is entirely insoluble in water, and can therefore be used for the purpose of separating iron and aluminium from manganese, zinc, nickel, and cobalt quantitatively.

Experiment 36. Make a neutral solution of ammonium succinate by neutralizing an aqueous solution of the acid, and boiling off all excess of ammonia. Add some of this solution to a solution known to contain manganese and iron in the ferric state. A brown-red precipitate will be formed. Filter and wash, and examine the filtrate for iron.

Isosuccinic acid, Ethylidene succinic acid, $\begin{matrix} CH(CO_2H)_2 \\ | \\ CH_3 \end{matrix}$.

This acid is made by treating α-cyan-propionic acid with an alkali. (What is α-cyan-propionic acid?)

Isosuccinic acid forms crystals which melt at 130°. Heated above its melting-point it breaks up into propionic acid and carbon dioxide: —

$$\begin{array}{l} CH(CO_2H)_2 \\ | \\ CH_3 \\ \text{Isosuccinic acid.} \end{array} = \begin{array}{l} CH_2.CO_2H \\ | \\ CH_3 \\ \text{Propionic acid.} \end{array} + CO_2.$$

NOTE FOR STUDENT. — Notice carefully the difference between the two succinic acids, as shown by their conduct when heated. What is the difference?

Acids of the formula $C_5H_8O_4$[$= C_3H_6(CO_2H)_2$]. — Four acids of the formula $C_5H_8O_4$ are known, only one of which, however, need be mentioned here. This is, —

Pyrotartaric acid, $\begin{array}{l} CH_3.CH.CO_2H \\ | \\ CH_2.CO_2H \end{array}$. — As the name indicates, this acid may be made by dry distillation of tartaric acid.

TRI-ACID ALCOHOLS.

The existence of mon-acid alcohols corresponding to the mon-acid bases, like potassium hydroxide, and of di-acid alcohols corresponding to the di-acid bases, like calcium hydroxide, suggests the possible existence of *tri-acid alcohols* corresponding to tri-acid bases, like ferric hydroxide. There is only one alcohol of this kind derived from the paraffin hydrocarbons that is at all well known. This is the common substance glycerin or glycerol.

Glycerol, Glycerin, Propantriol, $C_3H_8O_3$. — As has been stated repeatedly, glycerol occurs very widely distributed as the alcoholic or basic constituent of the fats. The acids with which it is in combination are mostly members of the fatty acid series, though one, viz., *oleïc acid*, which is found frequently, is a member of another series. Besides oleïc acid the two acids most frequently met with in fats are palmitic and stearic acids. When a fat is saponified with caustic potash, it yields free glycerol and the potassium salts of the acids. The reactions in the case of the glycerol compounds of palmitic and stearic acids are these: —

Formation.

$$C_3H_5(OH)_3 + 3\,HO\,.\,OC\,.\,C_{15}H_{31} = C_3H_5(O\,.\,OC\,.\,C_{15}H_{31})_3 + 3\,H_2O.$$

Glycerol. Palmitic acid. Glycerol tri-palmitate, or Palmitin.

$$C_3H_5(OH)_3 + 3\,HO\,.\,OC\,.\,C_{17}H_{35} = C_3H_5(O\,.\,OC\,.\,C_{17}H_{35})_3 + 3\,H_2O.$$

Glycerol. Stearic acid. Glycerol tri-stearate, or Stearin.

Saponification.

$$C_3H_5(O\,.\,OC\,.\,C_{15}H_{31})_3 + 3\,KOH = C_3H_5(OH)_3 + 3\,C_{15}H_{31}\,.\,CO_2K.$$

Palmitin. Glycerol. Potassium palmitate.

$$C_3H_5(O\,.\,OC\,.\,C_{17}H_{35})_3 + 3\,KOH = C_3H_5(OH)_3 + 3\,C_{17}H_{35}\,.\,CO_2K.$$

Stearin. Glycerol. Potassium stearate.

The fats are also decomposed by superheated steam, yielding free glycerol and the free acids, and this method is used on the large scale, a little lime being added to facilitate the process. Lead oxide decomposes fats yielding a mixture of glycerol and the lead salts of the acids. The mixture is known in medicine as "lead plaster."

Glycerol is formed in small quantity by the alcoholic fermentation of sugar.

It has been made synthetically from propylene chloride, $C_3H_6Cl_2$. The necessary steps are: (1) treatment with chlorine, giving $C_3H_5Cl_3$; (2) treatment of the tri-chlorine derivative with water, thus replacing the three chlorine atoms by hydroxyl.

Glycerol is a thick colorless liquid, with a sweetish taste (compare with glycol). It mixes with alcohol and water in all proportions but is insoluble in ether. It attracts moisture from the air. At low temperatures it solidifies, forming deliquescent crystals which melt at 17°. Pure glycerol boils at 290° without decomposition. If salts are present it undergoes decomposition at the boiling temperature. Under diminished pressure it can be distilled; but, if heated to its boiling-point under the ordinary atmospheric pressure, it undergoes decomposition. It is volatile with water vapor.

Glycerol is used to some extent in medicine, but its chief use is in the manufacture of *nitro-glycerin.*

Experiment 37. Heat a little commercial glycerol in a dry vessel, and try to boil it. What evidence have you that it undergoes decomposition? Put 20cc to 30cc glycerol in 400cc to 500cc water in a flask; connect with a condenser, and boil. Prove that glycerol passes over with the water vapor.

The reactions of glycerol all clearly lead to the conclusion that it is a tri-acid alcohol.

(1) The three hydroxyl groups can be replaced successively by chlorine, giving the compounds, —

Chlorhydrin, $C_3H_5\begin{cases}Cl\\(OH)_2\end{cases}$;

Dichlorhydrin, $C_3H_5\begin{cases}Cl_2\\OH\end{cases}$;

and *Trichlorhydrin*, $C_3H_5Cl_3$,

which last compound is propane in which three hydrogen atoms are replaced by chlorine, or trichlorpropane.

(2) It forms three classes of ethereal salts containing one, two, and three acid residues respectively. For example, with acetic anhydride these reactions take place: —

1. $C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + (C_2H_3O)_2O = C_3H_5\begin{cases}O.C_2H_3O\\OH\\OH\end{cases} + C_2H_4O_2.$

2. $C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 2\,(C_2H_3O)_2O = C_3H_5\begin{cases}OC_2H_3O\\OC_2H_3O\\OH\end{cases} + 2\,C_2H_4O_2.$

3. $C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3\,(C_2H_3O)_2O = C_3H_5\begin{cases}OC_2H_3O\\OC_2H_3O\\OC_2H_3O\end{cases} + 3\,C_2H_4O_2.$

In regard to the relations of the hydroxyl groups to the parts of the radical C_3H_5, we have very little experimental evidence, though it appears highly probable that each hydroxyl is in combination with a different carbon atom as represented in the formula $\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}$.

In the first place, we have seen above that compounds containing two hydroxyls in combination with the same carbon are not readily formed, if they are formed at all, and we have had some reason for concluding that this kind of combination is impossible. It would follow from this that the simplest tri-acid alcohol must contain at least three atoms of carbon, just as the simplest di-acid alcohol must contain at least two atoms of carbon. We have seen that the simplest tri-acid alcohol known does contain three atoms of carbon.

Further, if the formula of glycerol is $\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}$, it contains two primary alcohol groups, CH_2OH, and we have seen that this group is converted into carboxyl under the influence of oxidizing agents. Therefore, we should expect by oxidizing glycerol to get products of the formulas, $\begin{matrix}CO_2H\\|\\CHOH\\|\\CH_2OH\end{matrix}$, and $\begin{matrix}CO_2H\\|\\CHOH\\|\\CO_2H\end{matrix}$. Such products actually are obtained, the first being *glyceric acid* (which see), and the second *tartronic acid* (which see).

Just as ethyl alcohol is regarded as water in which one hydrogen is replaced by the univalent radical C_2H_5, as $\begin{matrix}C_2H_5\\H\end{matrix}\}O$; and glycol is regarded as water in which two hydrogen atoms of two molecules of water are replaced by the bivalent radical C_2H_4, as $\begin{matrix}H\\H\end{matrix}>C_2H_4>O$; so also glycerol may be regarded as water in which three hydrogen atoms of three molecules are replaced by the *trivalent radical* C_3H_5, thus: —

H.OH	
H.OH	$C_3H_5\{$ OH
H.OH	OH.
	OH
Three molecules water.	Glycerol.

Ethereal salts or esters of glycerol. — Among the important esters of glycerol are the *nitrates*. Two of these are known; viz., the *mono-nitrate*, $C_3H_5\begin{cases}O.NO_2\\OH\\OH\end{cases}$, and the *tri-nitrate*, $C_3H_5(ONO_2)_3$, the latter being the chief constituent of *nitro-glycerin*. Nitro-glycerin is prepared by treating glycerol with a mixture of concentrated sulphuric and nitric acids. It is a pale yellow oil which is insoluble in water. At $-20°$ it crystallizes in long needles. It explodes very violently by concussion. It can be burned in an open vessel, but if heated quickly it explodes. It also explodes by percussion. *Dynamite* is infusorial earth impregnated with nitro-glycerin. Mixed with nitrocellulose (which see) it forms *smokeless powder*. It is the active constituent of other explosives.

When treated with a caustic alkali, nitro-glycerin is saponified, yielding glycerol and a nitrate. This shows that it is an ester of nitric acid, and not a nitro-compound.

Fats. — The relation of the fats to glycerol has already been stated. Most fats are mixtures of the three neutral esters which glycerol forms with palmitic, stearic, and oleïc acids, and which are known by the names *palmitin*, *stearin*, and *oleïn*. *Oleïn* is liquid, and the other two fats are solids, stearin having the higher melting-point. Therefore, the larger the proportion of oleïn contained in a fat, the softer it is, while the greater the proportion of stearin, the higher its melting-point. Among the fats which are particularly rich in stearin may be mentioned *mutton tallow*, *beef tallow*, and *lard*. *Human fat* and *palm oil* are particularly rich in palmitin. *Sperm oil* and *cod-liver oil* are rich in oleïn. Fats occur very widely distributed in nature, both in plants and animals. They are of the highest importance from the physiological point of view, forming one of the three great classes of food-stuffs.

Butter consists of ethereal salts of glycerol and the following acids: myristic, palmitic, and stearic acids, which are not

volatile, and butyric, caproïc, caprylic, and capric acids, which are volatile with water vapor. All the acids mentioned are members of the fatty acid series. Some of these acids are soluble and some are insoluble in water. The percentage of insoluble fatty acids contained in butter has been found to be 88 per cent. As the proportion of insoluble fatty acids contained in artificial butters, such as the so-called *oleo-margarin*, is greater than that contained in butter, it is not a difficult matter to distinguish between the two by determining the amount of these acids contained in them.

Tri-basic Acids.

Tri-carballylic acid, $C_3H_5(CO_2H)_3$. — This acid can be made from trichlorhydrin, $C_3H_5Cl_3$ (which see), by replacing the chlorine by cyanogen, and heating with an alkali the *tri-cyanhydrin* thus obtained. It can be made also by treating aconitic acid (which see) with nascent hydrogen. It crystallizes from water in rhombic prisms which melt at 157° to 158°.

Tetr-acid Alcohols.

Erythrol, Erythrite, $C_4H_{10}O_4[= C_4H_6(OH)_4]$. — This substance occurs in one of the algæ (*Protococcus vulgaris*) and in several lichens. It crystallizes from water in quadratic prisms. It has a very sweet taste. The fact that the simplest tetr-acid alcohol contains four atoms of carbon should be specially noted.

There is no well known *tetra-basic acid* derived from the hydrocarbons of the paraffin series.

Pent-acid Alcohols.

One pent-acid alcohol occurs in nature in *Adonis vernalis*, and it is hence called *adonite*. It is also formed by reduction of rhamnose (which see).

By reduction of xylose (which see) a pent-acid alcohol, called *xylite*, is formed; and by reduction of arabinose (which see) another called *arabite* is formed.

All the above named alcohols have the formula $C_5H_{12}O_5$[= $C_5H_7(OH)_5$]. There are three modifications of arabite — two optically active, and one inactive. There is still another pent-acid alcohol known as *rhamnite*, formed by reduction of rhamnose (which see). This has the composition represented by the formula $C_6H_{14}O_5$[= $CH_3.C_5H_6(OH)_5$].

Two pentabasic acids have been made, but they are of no special importance.

Hex-acid Alcohols.

There are several hex-acid alcohols known. Most of them are derived from hexane, and have the composition represented by the formula $C_6H_8(OH)_6$. It will be noticed that these *hex-acid alcohols* contain *six carbon atoms* each.

Mannitol, Mannite, $C_6H_8(OH)_6$. — Mannite is widely distributed in the vegetable kingdom. It occurs most abundantly in manna,[1] which is the partly dried sap of the manna-ash (*Fraxinus ornus*). It is obtained from incisions in the bark of the tree.

Mannite is formed in the lactic acid fermentation of sugar. It is formed also by the action of nascent hydrogen on fructose and mannose. It crystallizes in needles, or rhombic prisms, easily soluble in water and in alcohol. It has a sweet taste.

Nitric acid converts mannite into *manno-saccharic acid* (which see). When boiled with concentrated hydriodic acid, it is converted into secondary hexyl iodide, $C_6H_{13}I$.

Mannite hexa-nitrate (nitro-mannite), $C_6H_8(O.NO_2)_6$, is formed by treating mannite with a mixture of concentrated sulphuric and nitric acids. It is a solid substance and is very explosive. (Analogy with nitro-glycerin.)

[1] The manna of the Scriptures was obtained from the branches of *Tammarix gallica*. It contained no mannite, but a substance of similar properties.

Mannite hex-acetate, $C_6H_8(O.C_2H_3O)_6$, is formed by treating mannite with *acetic anhydride*. Its formation, as well as that of the hexa-nitrate, shows that mannite is a hex-acid alcohol. *The number of acetyl groups that enter into a compound when it is treated with acetic anhydride shows how many hydroxyl groups are in the compound.*

There are three varieties of mannite — the ordinary, known as *dextro-mannite*, and, further, *levo-mannite*, and *inactive mannite*.

Dulcite, $C_6H_8(OH)_6$. — This occurs in a kind of manna obtained from Madagascar, the source of which, however, is unknown. It is formed by treating sugar of milk or galactose with nascent hydrogen (compare with mannite in this respect).

Nitric acid oxidizes dulcite, forming mucic acid (which see), isomeric with manno-saccharic acid, which is formed from mannite. Like mannite, when boiled with hydriodic acid it yields secondary hexyl iodide, $C_6H_{13}I$.

Sorbite, $C_6H_8(OH)_6$. — Ordinary sorbite occurs in the berries of the mountain ash, and in many other fruits, as plums, cherries, apples, etc. It is formed by reduction of glucose, and also together with mannite by the reduction of fructose. This variety is known as dextro-sorbite, because it is formed from glucose, which is dextro-rotatory. *Levo-sorbite* is also known, having been obtained by the reduction of levo-gulose.

There are no *hexa-basic acids* known belonging to this series.

Hept-acid Alcohols, etc.

Perseite, $C_7H_9(OH)_7$, occurs in the fruit and leaves of *Laurus persea*, and has been made artificially from *dextro-mannose*, by treating it with hydrocyanic acid, converting the nitril thus formed into the corresponding acid, and reducing this acid. It is also called *dextro-mannoheptite*. By similar reactions an oct-acid and a non-acid alcohol have been made from glucose.

CHAPTER X.

MIXED COMPOUNDS. — DERIVATIVES OF THE PARAFFINS.

Under this head are included compounds that belong at the same time to two or more of the chief classes already studied. Thus, there are substances which are at the same time alcohols and acids. There are others which are at the same time alcohols and aldehydes, alcohols and ketones, acids and ketones, etc. Fortunately, for our purpose, the number of compounds of this kind actually known is comparatively small, though among them are many of the most important natural compounds of carbon. The first class that presents itself is that of the *alcohol acids* or *acid alcohols;* that is, substances that combine within themselves the properties of both alcohol and acid. They are commonly called *oxy-acids* or *hydroxy-acids.*

Hydroxy-acids, $C_nH_{2n}O_3$.

These acids may be regarded either as monobasic acids into which one alcoholic hydroxyl has been introduced, or as monacid alcohols into which one carboxyl has been introduced. As their acid properties are more prominent than the alcoholic properties, they are commonly referred to the acids. Running parallel, then, to the series of fatty acids, we may look for a series of hydroxy-acids, each of which differs from the corresponding fatty acid by one atom of oxygen, or by containing one hydroxyl in the place of one hydrogen, thus: —

	Fatty acids.	Hydroxy-acids.
Formic acid . . .	$H.CO_2H$	$HO.CO_2H$.
Acetic acid . . .	$CH_3.CO_2H$	$CH_2<\begin{matrix}OH\\CO_2H\end{matrix}$.
Propionic acid . .	$C_2H_5.CO_2H$	$C_2H_4<\begin{matrix}OH\\CO_2H\end{matrix}$.
	etc.	etc.

The first member of the series, which by analogy would be called *hydroxy-formic acid*, is nothing but the ordinary hypothetical carbonic acid. Although its relation to formic acid is the same as that of the next member of the series to acetic acid, it certainly has no properties in common with the alcohols; but, owing to its peculiar structure, it is a dibasic acid which the other members of the series are not. Nevertheless, it may be referred to here for the sake of a few of its derivatives, which are somewhat allied to those of the hydroxy-acids proper.

Carbonic acid, $H_2CO_3\left(CO<\begin{matrix}OH\\OH\end{matrix}\right)$. — It is believed that this body exists in solutions of carbon dioxide in water. All that is known about it is that it is a feeble dibasic acid, and breaks up into water and carbon dioxide whenever it is set free from its salts. We have seen that this instability is generally met with in compounds containing two hydroxyls in combination with one carbon atom.

Among the derivatives of carbonic acid which may be mentioned at this time are the ethereal salts. These may be made: —

1. By treating silver carbonate, $CO<\begin{matrix}OAg\\OAg\end{matrix}$, with the iodides of alcohol radicals; as, for example, —

$$CO<\begin{matrix}OAg\\OAg\end{matrix} + 2\,C_2H_5I = CO<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + 2\,AgI.$$

2. By treating the alcohols with carbonyl chloride, $COCl_2$: —

$$COCl_2 + 2\,C_2H_5OH = CO(OC_2H_5)_2 + 2\,HCl.$$

Ethyl chlor-carbonate, $OC<^{Cl}_{OC_2H_5}$. — This compound is made by treating alcohol with carbonyl chloride: —

$$COCl_2 + C_2H_5OH = OC<^{Cl}_{OC_2H_5} + HCl.$$

It may be regarded as the ethyl ester of mono-chlor-formic acid, Cl.COOH; and, properly speaking, should be called *ethyl chlor-formate.*

Carbon disulphide acts very much like carbon dioxide towards alkalies and alcohols, and thus a number of ether acids and ethereal salts containing sulphur can be made. Thus, when carbon disulphide is added to a solution of caustic potash in alcohol, a potassium salt of the formula $SC<^{OC_2H_5}_{SK}$ is formed. This is called *potassium xanthogenate.* Free xanthogenic acid is very unstable, breaking up into alcohol and carbon disulphide. The formation of the salt is represented by the following equation: —

$$CS_2 + KOH + C_2H_5OH = SC<^{OC_2H_5}_{SK} + H_2O.$$

A similar salt made from ordinary amyl alcohol has been used for the purpose of destroying *phylloxera*, the insect, which is so destructive to grape-vines, particularly in the wine districts of France.

General methods for the preparation of hydroxy-acids. The methods available for making the hydroxy-acids are modifications of those used for making alcohols and acids.

Starting with a mon-acid alcohol, we can make a hydroxy-acid by the same methods which we used in making an acid from a hydrocarbon. Suppose, for example, that we are to make acetic acid from marsh gas. The reactions which we make use of are: (1) the preparation of a halogen derivative; (2) conversion of the halogen derivative into the cyanogen

derivative; and (3) conversion of the cyanogen derivative into the acid. We describe the results of these operations by saying that we have introduced carboxyl. By similar operations we can introduce carboxyl into methyl alcohol, and the product is hydroxy-acetic acid.

It is, however, generally better to start with an acid, and introduce hydroxyl. This can be done in several ways: —

1. By treating a halogen derivative of an acid with water or silver hydroxide: —

$$CH_2{<}\begin{matrix}Br\\CO_2H\end{matrix} + HHO = CH_2{<}\begin{matrix}OH\\CO_2H\end{matrix} + HBr.$$

Brom-acetic acid.

2. By treating an *amino derivative* of an acid with nitrous acid (see page 99): —

$$CH_2{<}\begin{matrix}NH_2\\CO_2H\end{matrix} + HNO_2 = CH_2{<}\begin{matrix}OH\\CO_2H\end{matrix} + N_2 + H_2O.$$

Amino-acetic acid.

3. By treating a *sulphonic-acid* derivative of an acid with caustic potash: —

$$CH_2{<}\begin{matrix}SO_2OH\\CO_2H\end{matrix} + KOH = CH_2{<}\begin{matrix}OH\\CO_2H\end{matrix} + KHSO_3.$$

Sulpho-acetic acid.

The first two of these reactions have been described and mentioned as affording methods for the introduction of hydroxyl into hydrocarbons. It will be seen that the only difference between the reactions used in making alcohols and those used in making hydroxy-acids is that in one case we start with the hydrocarbons, while in the other we start with the acids.

Glycolic acid, Hydroxy-acetic acid, Oxy-acetic acid, Ethanolic acid, $C_2H_4O_3\left(= CH_2{<}\begin{matrix}OH\\CO_2H\end{matrix}\right)$. — Glycolic acid is found in nature in unripe grapes, and in the leaves of the wild grape (*Ampelopsis hederacea*).

It can be made from glycocoll, which is amino-acetic acid (see reaction 2, above), from brom- or chlor-acetic acid and water (see reaction 1, above), and by the oxidation of glycol: —

$$\underset{\text{Glycol.}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + O_2 = \underset{\text{Glycolic acid.}}{\begin{matrix}CO_2H\\|\\CH_2OH\end{matrix}} + H_2O.$$

This consists in transforming one of the primary alcohol groups, CH_2OH, contained in glycol into carboxyl. (What would be formed by conversion of both the primary alcohol groups of glycol into carboxyl?) It can also be made by careful oxidation of ethyl alcohol with nitric acid. For this purpose a mixture of alcohol and nitric acid is allowed to stand until no further action takes place.

Glycolic acid forms crystals that are easily soluble in water, alcohol, and ether.

As an acid, glycolic acid forms a series of salts with metals, and ethereal salts with alcohol radicals. The latter, of which ethyl glycolate may be taken as an example, can be made by means of one of the reactions usually employed for making ethereal salts; for example, by treating silver glycolate with ethyl iodide: —

$$CH_2 < \begin{matrix}OH\\CO_2Ag\end{matrix} + C_2H_5I = CH_2 < \begin{matrix}OH\\CO_2C_2H_5\end{matrix} + AgI.$$

In this reaction, as well as in the formation of salts of glycolic acid, the alcoholic hydroxyl remains unchanged.

As an alcohol, glycolic acid forms ethers of which *ethyl-glycolic acid*, $CH_2 < \begin{matrix}OC_2H_5\\CO_2H\end{matrix}$, may serve as an example. It will be seen that this is isomeric with ethyl glycolate. But while the latter has alcoholic properties, the former has acid properties. Ethyl glycolate is a liquid which boils at 160°. Ethyl-glycolic acid is a liquid which boils at 206° to 207°. Finally, as an alcohol, glycolic acid forms ethereal salts, of which acetyl-glycolic acid may serve as an example. This is glycolic acid

in which the hydrogen of the hydroxyl is replaced by acetyl, $CH_2 < \begin{matrix} O.C_2H_3O \\ CO_2H \end{matrix}$, bearing, as will be seen, the same relation to glycolic acid and acetic acid that ethyl acetate, $C_2H_5.O.C_2H_3O$, bears to alcohol and acetic acid.

Glycolic acid and some of the other acids of the series lose water when heated, and yield peculiar anhydrides. The product obtained from glycolic acid is called *glycolide*. It has neither acid nor alcoholic properties, and is, therefore, believed to be derived from glycolic acid as represented in this equation: —

$$2\,CH_2 < \begin{matrix} OH \\ COOH \end{matrix} = \begin{matrix} CH_2 - O - CO \\ | \qquad\quad | \\ CO - O - CH_2 \end{matrix} + 2\,H_2O.$$

Glycolide.

Glycolide is insoluble in cold water. When boiled for a long time with water, it is converted into glycolic acid.

Lactic acids, Hydroxy-propionic acids, Oxy-propionic acids, $C_3H_6O_3\left(= C_2H_4 < \begin{matrix} OH \\ CO_2H \end{matrix}\right)$. — In speaking of propionic acid, it was pointed out that two series of substitution-products of the acid are known, which are designated as the α- and β-series. Accordingly we should expect to find two hydroxy-propionic acids, the α- and the β-acid. Two lactic acids have been known for a long time. One of these is *ordinary lactic acid;* the other a variety which is found in flesh, and hence called *sarco-lactic acid*. But, strange to say, a thorough investigation of these two acids has proved that both must be represented by the same structural formula, as both conduct themselves in exactly the same way towards reagents. Further, two other hydroxy-propionic acids are certainly known. The facts then are these: four acids are known, all of which are hydroxy-propionic acids. Our theory enables us to foretell the existence of only two. Before discussing this apparent discrepancy let us briefly study the acids themselves.

1. **Lactic acid, inactive Ethylidene-lactic acid, α-Hydroxy-propionic acid,** $CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}$. — Lactic acid is made by the fermentation of sugar, as has already been described under Butyric Acid (which see). The process is carried out best by dissolving cane sugar and a little tartaric acid in water; then adding putrid cheese, milk, and zinc carbonate, the object of which is to prevent the solution from becoming acid, as the presence of free acid is fatal to the ferment. Lactic acid can also be made by fermentation of sugar of milk, and is hence contained in sour milk; by boiling α-chlor-propionic acid with alkalies, —

$$CH_3.CH<\begin{matrix}Cl\\CO_2H\end{matrix}+KOH=CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}+KCl;$$

and by treating alanine (α-amino-propionic acid) with nitrous acid, —

$$CH_3.CH<\begin{matrix}NH_2\\CO_2H\end{matrix}+HNO_2=CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}+N_2+H_2O.$$

Lactic acid is a thick liquid that mixes with water and with alcohol in all proportions.

When commercial lactic acid of specific gravity 1.21 is distilled under much diminished pressure (1 mm. of mercury) and the distillate allowed to stand in a freezing-mixture for a time, it takes the form of crystals which melt at 17°.5–18°.

Treated with hydriodic acid, it is reduced to propionic acid.

$$CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}+2\,HI=CH_3.CH_2.CO_2H+H_2O+I_2.$$

2. **Sarco-lactic acid, dextro-ethylidene-lactic acid,** $CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}$. — This acid occurs in the liquids expressed from meat. It is therefore contained in "extract of meat," and can be obtained most readily from this source.

Its properties are, for the most part, like those of inactive lactic acid, and its conduct towards reagents is in all respects the same. Its salts are somewhat more easily soluble than those of ordinary inactive lactic acid. The chief difference between the two is observed in the action towards polarized light. Dextro-lactic acid turns the plane of polarization to the right. Its salts are all levo-rotatory. On the other hand, neither inactive lactic acid nor its salts exert any action upon polarized light.[1]

3. **Levo-lactic acid,** $CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}$. — A third variety of ethylidene-lactic acid, which turns the plane of polarization to the left, is formed from cane sugar by the action of a certain ferment found in a spring-water. By fractional crystallization of the strychnine salt of ordinary inactive lactic acid two kinds of crystals are obtained. The acid separated from one kind is sarco-lactic, or dextro-lactic, acid; while that separated from the other kind is levo-lactic acid. This method of splitting the inactive acid into the two active varieties is applicable to many other similar cases. The relations between these three acids are of the same kind as those existing between the three varieties of tartaric acid.

4. **Hydracrylic acid,**
β-Hydroxy-propionic acid, $\left.\begin{matrix}CH_2OH\\|\\CH_2.CO_2H\end{matrix}\right.$.

Hydracrylic acid is made by boiling β-iodo-propionic acid with water or silver oxide and water: —

$$\begin{matrix}CH_2I\\|\\CH_2.CO_2H\end{matrix} + HHO = \begin{matrix}CH_2.OH\\|\\CH_2.CO_2H\end{matrix} + HI.$$

It is made also by starting with ethylene, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. When this hydrocarbon is treated with hypochlorous acid, HOCl, it is con-

[1] See active and inactive amyl alcohols, p. 126.

verted into ethylene-chlorhydrine, $\begin{matrix}CH_2Cl\\|\\CH_2OH\end{matrix}$ (which see). By replacing the chlorine with cyanogen, and boiling the cyanhydrine, $\begin{matrix}CH_2OH\\|\\CH_2CN\end{matrix}$, thus obtained, with an alkali, hydracrylic acid is obtained.

These reactions clearly show that hydracrylic acid is an ethylene compound, and, as it is made from β-iodo-propionic acid by replacing the iodine with hydroxyl, it follows further that the β-substitution-products of propionic acid are ethylene products, and that the α-products are ethylidene products (see p. 131).

Hydracrylic acid is a syrup. Its salts differ markedly from those of the inactive and active lactic acids. When heated, it loses water and is transformed into *acrylic acid*, $CH_2.CH.CO_2H$ (which see).

The difference in conduct between ethylidene-lactic acid and ethylene-lactic acid, when heated, is interesting and suggestive. When ethylidene-lactic acid is heated, both its acid and alcoholic properties are destroyed, both the alcoholic and acid hydroxyls taking part in the reaction. Whereas, when ethylene-lactic acid is heated, only the alcoholic properties are destroyed, the carboxyl remaining intact.

There are then more hydroxy-propionic acids known than our theory of linkage in its simplest form can account for. Other cases of this kind are known, and one very marked and especially interesting one will be taken up when tartaric acid is treated of. It will be shown that just as there are two active lactic acids and an inactive one, so there are two active tartaric acids and an inactive one, which conduct themselves in the same way towards reagents, and must hence be represented by the same structural formula.

We have here to deal with a new kind of isomerism. Bodies may conduct themselves chemically in exactly the same way,

and yet differ in some of their physical properties, as in their action towards polarized light. To distinguish this kind of isomerism from ordinary chemical isomerism it has been called *physical isomerism.*

An ingenious hypothesis has been put forward by way of explanation of that particular kind of physical isomerism which shows itself in the action of compounds upon polarized light. It must be remembered that our ordinary formulas have nothing whatever to do with the relations of the atoms and groups in space. They indicate *chemical relations* which are discovered by a study of *chemical reactions.*

Let us suppose that in a carbon compound one carbon atom is situated at the centre of a tetrahedron, and that the four atoms or groups which it holds in combination are at the angles of the tetrahedron, as represented in Fig. 10.

If these groups are all different in kind, and only in this case, it is possible to arrange them in two ways with reference to the carbon atom. The difference between the two arrange-

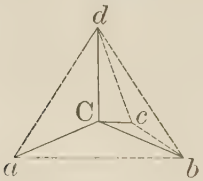


Fig. 10.

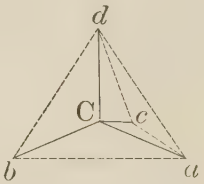


Fig. 11.

ments is that which is observed between either one and its reflection in a mirror. Imperfectly the second arrangement is shown in Fig. 11.[1]

A carbon atom, in combination with four different kinds of atoms or groups, is called an *asymmetrical carbon atom.* Whenever, therefore, a compound contains an asymmetrical carbon

[1] This can be made clear only by means of models. These can easily be made of stout wire and wooden balls.

atom, there are two possible arrangements of its parts in space which correspond to the two complementary tetrahedrons, viz., the *right-handed* and the *left-handed tetrahedron*.

In ethylidene lactic acid there is an asymmetrical carbon atom, as shown by the ordinary formula, which may be written thus:

$$CH_3 - \underset{\displaystyle CO_2H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH,$$

the central carbon atom appearing in combination with (1) hydrogen, (2) hydroxyl, (3) carboxyl, and (4) methyl. Hence, according to the hypothesis just stated, there ought to be two possible arrangements of the parts of a compound containing this group, one corresponding to the right-handed tetrahedron, the other to the left-handed tetrahedron. Both would be *ethylidene-lactic acids*. The inactive variety is formed by the combination of the two active varieties, and must, therefore, have a greater molecular weight than these.

The branch of chemistry which has to deal with the kind of isomerism just referred to is called *stereo-chemistry*. The phenomena of stereo-chemistry have been the subject of extensive investigation, and the facts established furnish a strong foundation for the theory briefly expounded above.

Hydroxy-sulphonic acids. — It has been pointed out that the sulphonic acids and the carbonic acids are analogous: that, for example, methyl-sulphonic acid, $CH_3.SO_3H$, is analogous to methyl-carbonic or acetic acid, $CH_3.CO_2H$. Now, just as the hydroxy-acids already treated of are derived from the carbonic acids by the introduction of hydroxyl, so there are hydroxy acids derived in a similar way from the sulphonic acids. Only one such acid is well known. It is —

Isethionic acid, $C_2H_4{<}\overset{\displaystyle OH}{\underset{\displaystyle SO_3H}{}}$, also called *β-hydroxy-ethyl-sulphonic acid*. In composition it is analogous to the hydroxy-propionic acids. It is prepared by passing sulphur trioxide into

well cooled alcohol or ether and boiling the product with water; and also by treating taurine (which see) with nitrous acid:

$$\begin{matrix} CH_2.NH_2 \\ | \\ CH_2.SO_3H \end{matrix} + HNO_2 = \begin{matrix} CH_2OH \\ | \\ CH_2.SO_3H \end{matrix} + H_2O + N_2.$$

Lactones.

The monohydroxy-monobasic acids of the paraffin series are designated as α-, β-, γ-, δ-, etc., acids, according to the position of the hydroxyl with reference to the carboxyl. When the hydroxyl is united with the carbon atom with which the carboxyl is united the product is called an α-hydroxy-acid. When the hydroxyl is united with the next carbon atom in the chain the product is called a β-hydroxy-acid, etc. The following examples will make this clear: —

Acids of the formulas

$CH_2(OH).CO_2H$, $CH_3.CH(OH).CO_2H$, $CH_3.CH_2.CH(OH).CO_2H$

are α-hydroxy-acids.

Acids of the formula

$CH_2(OH).CH_2.CO_2H$, $CH_3.CH(OH).CH_2.CO_2H$,
$CH_3.CH_2.CH(OH).CH_2.CO_2H$ are β-hydroxy-acids.

Acids of the formulas

$CH_2(OH).CH_2.CH_2.CO_2H$, etc., are γ-hydroxy-acids.

Similarly an acid of the formula

$CH(OH).CH_2.CH_2.CH_2.CO_2H$ is called a δ-hydroxy-acid.

The γ- and δ-acids differ from the others in this respect that they lose the elements of water when set free from their salts. Thus, when a salt of γ-hydroxy-butyric acid in solution is treated with a mineral acid, a neutral compound is precipitated and not the acid corresponding to the salt. The compound thus formed is called a *lactone*. The reaction between sodium

γ-hydroxy-butyrate and hydrochloric acid is represented by the following equation: —

$$\begin{aligned} &CH_2(OH).CH_2.CH_2.CO_2Na + HCl \\ &= CH_2.CH_2.CH_2.CO + NaCl + H_2O. \\ &\quad\quad\quad

Glyceric acid, Propandiolic acid, $C_3H_6O_4$ $\left[\begin{array}{l} CH_2OH \\ | \\ =CHOH \\ | \\ CO_2H \end{array}\right]$.—

This acid has been referred to as the first product of the oxidation of glycerol. It is prepared by allowing glycerol and nitric acid to stand together at the ordinary temperature for some time, and then heating on the water-bath. It can also be made by treating β-chlor-lactic acid with water.

An optically active variety of glyceric acid has been obtained from the inactive variety. It will be seen that the acid contains an asymmetric carbon atom.

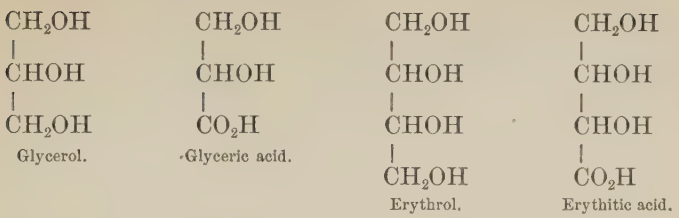
Glyceric acid is a thick syrup which mixes with water and alcohol. When treated with very concentrated hydriodic acid, it is converted into β-iodo-propionic acid. This conversion involves two reactions:—

$$(1) \qquad \begin{array}{l} CH_2OH \\ | \\ CHOH + \\ | \\ CO_2H \end{array} \quad HI = \begin{array}{l} CH_2I \\ | \\ CHOH + H_2O, \text{ and} \\ | \\ CO_2H \end{array}$$

$$(2) \qquad \begin{array}{l} CH_2I \\ | \\ CHOH + 2\ HI = \\ | \\ CO_2H \end{array} \quad \begin{array}{l} CH_2I \\ | \\ CH_2 \quad + H_2O + 2\ I. \\ | \\ CO_2H \end{array}$$

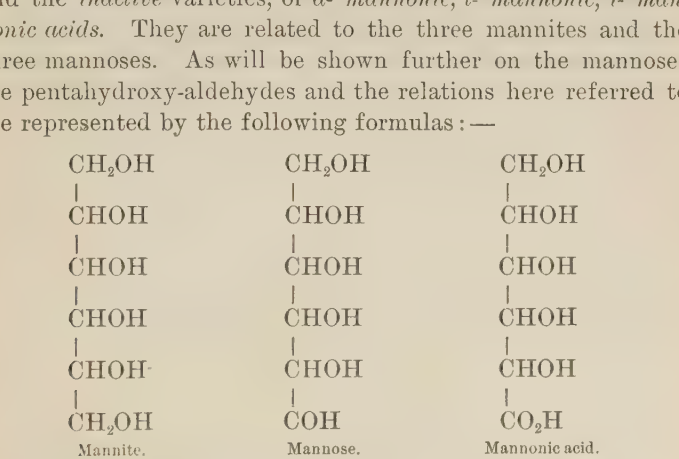
Other Hydroxy-monobasic Acids.

Just as by oxidation of the tri-acid alcohol glycerol, a dihydroxy-monobasic acid can be formed, so by oxidation of the tetr-acid alcohol, erythrol, a trihydroxy-monobasic acid can be formed. This is *erythritic acid*. Its relation to erythrol is like that of glyceric acid to glycerol:—



Similarly from the pent-acid alcohols tetrahydroxy-monobasic acids, and from the hex-acid alcohols, pentahydroxy-monobasic acids can be made. The latter are of special importance on account of their connection with the sugars.

Mannonic acids, $C_6H_{12}O_7 (= C_5H_6(OH)_5CO_2H)$. — Three acids are included in this group. They are the *dextro*, the *levo*, and the *inactive* varieties, or *d*-[1]*mannonic*, *l*-[1]*mannonic*, *i*-[1]*mannonic acids*. They are related to the three mannites and the three mannoses. As will be shown further on the mannoses are pentahydroxy-aldehydes and the relations here referred to are represented by the following formulas: —



The difference between the three mannonic acids is of the same kind as that between the three lactic acids. The dextro and levo varieties are complementary forms, while the inactive variety is formed by a combination of the dextro and levo varieties.

[1] Instead of using the prefixes *dextro-* and *levo-*, and the word *inactive*, it is customary to use the letters *d-*, *l-*, and *i-* as they are here used.

Gluconic acids, $C_6H_{12}O_7 (= C_5H_6(OH)_5CO_2H)$. — The gluconic acids are related to the three glucoses in the same way that the mannonic acids are related to the mannoses. *Dextrogluconic acid* is formed by the oxidation of glucose and of cane sugar. When heated with quinoline to 140°, it is partly converted into *d*-mannonic acid. Similarly *d*-mannonic acid is partly converted into *d*-gluconic acid by the same process. Three **Gulonic acids** and three **Galactonic acids** of the same composition and structure as the mannonic and the gluconic acids are also known.

The existence of so many acids of the formula $C_5H_6(OH)_5CO_2H$ is due to the fact that a substance made up as represented in the formula

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CO_2H \end{array}$$

contains four asymmetric carbon atoms, each one of which carries with it the possibility of the existence of three varieties. This subject will be more fully discussed under the sugars.

Hydroxy-acids, $C_nH_{2n-2}O_5$.

The acids included under this head are *monohydroxy-dibasic acids*. They bear the same relation to the dibasic acids of the oxalic acid series that the simplest hydroxy-acids bear to the members of the formic acid series. The principal members of this series, and the only ones which will be treated of, are tartronic acid and malic acid.

Tartronic acid, $C_3H_4O_5\left(=CH(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — This acid is prepared by an indirect method from tartaric acid. It can be made, —

(1) By boiling brom-malonic acid with silver oxide and water: —

$$CHBr<\begin{matrix}CO_2H\\CO_2H\end{matrix} + AgOH = CH(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix} + AgBr;$$

(2) By treating brom-cyan-acetic acid with caustic potash: —

$$CHBr<\begin{matrix}CN\\CO_2H\end{matrix} + 2\,KOH + H_2O = CH(OH)<\begin{matrix}CO_2K\\CO_2H\end{matrix} + NH_3 + KBr.$$

Tartronic acid is a solid which crystallizes in prismatic crystals. It is easily soluble in water, alcohol, and ether. The anhydrous acid melts at 185–187° with evolution of carbon dioxide and water, and forms glycolide (which see): —

(1) $$CH(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix} = \underset{\text{Glycolic acid.}}{CH_2<\begin{matrix}OH\\CO_2H\end{matrix}} + CO_2.$$

(2) $$2\,CH_2<\begin{matrix}OH\\COOH\end{matrix} = \underset{\text{Glycolide.}}{\begin{matrix}CH_2-O-CO\\|\qquad\quad|\\CO-O-CH_2\end{matrix}} + 2\,H_2O.$$

Note for Student. — Compare reaction (1) with that which takes place when iso-succinic acid is heated, and note the analogy.

Hydroxy-succinic acids, $C_4H_6O_5\left(=C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — Three hydroxy-succinic acids have been described, the principal one being ordinary malic acid.

Malic acid, $C_4H_6O_5\left(=\begin{matrix}CH(OH).CO_2H\\|\\CH_2.CO_2H\end{matrix}\right)$. — This acid is very widely distributed in the vegetable kingdom, as in the berries of the mountain ash, in apples, cherries, etc.

It is best prepared from the berries of the mountain ash

which have not quite reached ripeness. The berries are pressed and boiled with milk of lime. The acid passes into solution as the calcium salt, and this is purified by crystallization.

It can also be made by treating aspartic acid, which is amino-succinic acid, $C_2H_3(NH_2) < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$, with nitrous acid, and by treating tartaric acid with hydriodic acid. This latter reaction will be explained when tartaric acid is considered. Tartaric and malic acids are closely related to each other, and both are related to succinic acid, as will appear from the reactions.

Malic acid is a solid substance which crystallizes with difficulty. It is very easily soluble in water and in alcohol. *Its solutions turn the plane of polarization to the right or to the left*, according to the concentration.

When heated it loses water and yields either fumaric or maleic acid (which see), according to the temperature. These acids are isomeric, and both are represented by the formula $C_2H_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$. The reaction mentioned is represented by the following equation: —

$$\underset{\text{Malic acid.}}{C_2H_3(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix}} = \underset{\text{Fumaric or maleïc acid.}}{C_2H_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}} + H_2O.$$

Note for Student. — Compare this reaction with that which takes place when hydracrylic acid is heated, and note the analogy.

When treated with hydriodic acid, malic acid is reduced to succinic acid.

Note for Student. — Compare this reaction with the conduct of lactic and glyceric acids when treated with hydriodic acid.

Treated with hydrobromic acid, malic acid is converted into mono-brom-succinic acid.

The reactions just described show clearly that malic acid is hydroxy-succinic acid. Nevertheless, if hydroxy-succinic acid is made by treating brom-succinic acid with silver oxide and

water, the product is not identical with ordinary malic acid, though the two resemble each other very closely. The acid thus obtained is —

Inactive malic acid, $C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}$. — Inactive malic acid can be made not only by the method first mentioned, but by several others, which indicate that the relation between it and succinic acid is that expressed in the formula given. It, like ordinary malic acid, is unquestionably a hydroxy-succinic acid, and both are derived from ordinary succinic acid.

Other reactions for the preparation of inactive malic acid are, —

(1) By treating dichlor-propionic acid with potassium cyanide, and boiling the product with caustic potash : —

$$CH_2Cl.CHCl.CO_2H + KCN = \begin{matrix}CH_2CN\\|\\CHCl.CO_2H\end{matrix} + KCl;$$

and

$$\begin{matrix}CH_2CN\\|\\CHCl.CO_2H\end{matrix} + 2\,KOH + H_2O = \begin{matrix}CH_2.CO_2K\\|\\CH(OH).CO_2H\end{matrix} + KCl + NH_3.$$

(2) By heating fumaric acid with water : —

$$C_2H_2<\begin{matrix}CO_2H\\CO_2H\end{matrix} + H_2O = C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix};$$ and

(3) By reduction of racemic acid with hydriodic acid. Racemic acid has the same composition as tartaric acid. The latter, when treated with hydriodic acid, yields active malic acid.

The properties of inactive malic acid are very much like those of active malic acid. As regards their chemical conduct

they are almost identical. The principal difference between them is observed in their conduct towards polarized light. They present a new case of *physical isomerism* of the same kind as that referred to in connection with the lactic acids (which see).

Dextro-malic acid. — Inactive malic acid bears the same relation to two active acids that inactive lactic acid bears to the two active varieties of that acid. When the cinchonine salt of inactive malic acid is subjected to fractional crystallization, two different salts are obtained. One of these is derived from ordinary *levo-malic acid*, while the other is derived from the isomeric *dextro-malic acid*.

Hydroxy-acids, $C_nH_{2n-2}O_6$.

These are *di-hydroxy-dibasic acids*. The chief members of the group are mesoxalic acid and the different modifications of tartaric acid.

Mesoxalic acid, $C_3H_2O_6\left(=C(OH)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — This acid is obtained by indirect and rather complicated reactions from uric acid (which see). It has been made also by boiling dibrom-malonic acid with baryta-water.

Note for Student. — Explain this reaction.

The acid forms deliquescent needles. When boiled it loses carbon dioxide and water, and glyoxylic acid, which is an aldehyde and acid related to oxalic acid, is formed: —

$$C(OH)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix} = \begin{matrix}CHO\\|\\CO_2H\end{matrix} + CO_2 + H_2O.$$

Glyoxylic acid.

This acid affords an example of a very rare condition; viz., the existence of a compound in which two hydroxyls are in combination with one and the same carbon atom.

Thursday

Di-hydroxy-succinic acids, $C_4H_6O_6$ $\left(= C_2H_2(OH)_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}\right)$.

1. Tartaric acid, $\begin{matrix} CH(OH).CO_2H \\ | \\ CH(OH).CO_2H \end{matrix}$. — Ordinary tartaric acid occurs very widely distributed in fruits, sometimes free, sometimes in the form of the potassium or calcium salt; as, for example, in grapes, berries of the mountain ash, potatoes, cucumbers, etc., etc.

It can be made by the following methods: —

(1) By oxidizing sugar of milk with nitric acid;

(2) Also by oxidizing cane sugar, starch, glucose, and other similar substances.

Tartaric acid is prepared from "tartar," which is impure acid potassium tartrate. When grape juice ferments this salt is deposited. It is purified by crystallization, converted into the calcium salt by treating it with chalk, and the calcium salt then decomposed by means of sulphuric acid.

The acid crystallizes in large monoclinic prisms, which are easily soluble in water and alcohol. It melts at 168–170°. *Its solution turns the plane of polarization to the right.*

Treated with hydriodic acid, tartaric acid yields first malic acid and then ordinary succinic acid: —

$$(1)\quad C_2H_2(OH)_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} + 2\,HI = \underset{\text{Malic acid.}}{C_2H_3(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix}} + H_2O + I_2;$$

$$(2)\quad C_2H_3(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix} + 2\,HI = \underset{\text{Succinic acid.}}{C_2H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}} + H_2O + I_2.$$

While malic acid is mono-hydroxy-succinic acid, ordinary tartaric acid appears to be di-hydroxy-succinic acid. But, just

as the malic acid prepared from mono-brom-succinic acid is optically inactive, and therefore different from natural, active malic acid, so too the tartaric acid prepared from di-brom-succinic acid is optically inactive, and therefore different from ordinary tartaric acid. The relations between the natural and the artificial acids will be considered more fully below.

Tartrates. Among the salts the following may be mentioned:

Mono-potassium tartrate, $KH.C_4H_4O_6$. This is the chief constituent of *tartar*. In pure form, as used in medicine, it is known as *cream of tartar*.

Sodium-potassium tartrate, $KNa.C_4H_4O_6 + 4\ H_2O$. This salt crystallizes very beautifully. It is known as *Rochelle salt* or *Seignette salt*. Seidlitz powders consist of (1) a mixture of Rochelle salt and sodium bicarbonate, and (2) tartaric acid. These are dissolved separately and then brought together, when a rapid evolution of carbon dioxide takes place.

Calcium tartrate, $Ca.C_4H_4O_6 + 4\ H_2O$. This salt occurs in senna leaves and in grapes. It forms a crystalline powder or rhombic octahedrons.

Potassium-antimonyl tartrate, $K(SbO).C_4H_4O_6 + \frac{1}{2}\ H_2O$. This is known as *tartar emetic*. It is prepared by digesting antimonic oxide with mono-potassium tartrate. It crystallizes in rhombic octahedrons. It loses its water of crystallization at 100°, and at 200 to 220° is converted into an antimony potassium salt of the formula $KSb.C_4H_2O_6$.

2. **Racemic acid**, $C_4H_6O_6 + H_2O$. — Racemic acid occurs, together with tartaric acid, in many kinds of grapes, and, on recrystallizing the crude tartar, acid potassium racemate, being more soluble than the tartrate, remains in the mother liquors. Racemic acid is formed by boiling ordinary tartaric acid with water, or with hydrochloric acid. If tartaric acid is heated with water in sealed tubes at 175°, it is almost completely transformed into racemic acid. It is formed further by oxidation of dulcite, mannite, cane sugar, gum, etc., with nitric acid. *It, together with a third variety of tartaric acid, known as*

inactive tartaric acid, is formed when dibrom-succinic acid is treated with silver oxide and water.

Racemic acid differs from tartaric acid in many ways. It crystallizes differently, and contains water of crystallization. It is less soluble than tartaric acid. It produces precipitates in solutions of lime salts, while tartaric acid does not. *Racemic acid is optically inactive*, while tartaric acid is dextro-rotatory. On the other hand, racemic and tartaric acids conduct themselves towards most reagents exactly alike.

The relations between racemic and tartaric acid are the same as those which have already been referred to as existing between inactive malic acid and dextro-malic acid, and between inactive lactic and dextro-lactic acid. This case is, however, of special interest, as it was the first one of the kind studied. The relations were discovered by means of the experiment described below.

When a solution of ammonium-sodium racemate,

$$(NH_4)Na.C_4H_4O_6,$$

is allowed to evaporate spontaneously, beautiful large crystals are deposited. On examining these carefully, they are found to be of two kinds. On the crystals of one kind certain hemihedral faces are developed, while on the crystals of the other kind the complementary hemihedral faces are developed; so that if a crystal of one kind is placed in front of a mirror, its reflection will represent the arrangement of the hemihedral faces met with on a crystal of the other kind. The crystals can be separated into *right-handed*, or those which have the right-handed hemihedral faces, and *left-handed*, or those which have the left-handed hemihedral faces.

On separating the acid from the right-handed crystals *it is found to be ordinary dextro-rotatory tartaric acid;* while the acid from the left-handed crystals is an isomeric substance called *lævo-rotatory tartaric acid.* When these two varieties of tartaric acid are brought together in solution, they unite, the action being attended by an elevation of temperature, and *the result is racemic acid.*

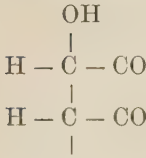
By crystallizing cinchonine racemate from alcohol it can be resolved into dextro and levo varieties, from which the corresponding active acids can be obtained.

We see thus that the *inactive* racemic acid consists of two optically active substances in combination, one of which, ordinary tartaric acid, is dextro-rotatory, and the other levo-rotatory.

As has already been stated, both inactive malic acid and inactive lactic acid have been resolved into two active varieties, one of which is dextro-rotatory, and the other levo-rotatory.

3. **Inactive tartaric acid, Mesotartaric acid,** $C_4H_4O_6 + H_2O$, is very similar to racemic acid. It is formed together with racemic acid by treating di-brom-succinic acid with silver oxide and water.

The tartaric acids contain two asymmetric carbon atoms,



. If the groups and atoms be arranged in the same way about both of them, the compound will be optically active, either dextro or levo rotatory. If arranged in the opposite way about both asymmetric carbon atoms, the complementary stereoisomeric form will result. A combination of the two active forms will give the inactive form.

On the other hand, the groups may be arranged in one way about one asymmetric carbon atom and in the other possible way about the other asymmetric carbon atom. The resulting compound will be inactive by internal compensation, and will not be capable of resolution into two active varieties. This latter arrangement is that of mesotartaric acid.

Hydroxy-acids, $C_nH_{2n-4}O_7$.

These are *mono-hydroxy-tribasic acids.* Citric acid is the only one known.

Citric acid, $C_6H_8O_7 + H_2O \left(= C_3H_4(OH) \begin{cases} CO_2H \\ CO_2H \\ CO_2H \end{cases} \right)$. — Citric acid, like malic and tartaric acids, is very widely distributed in nature in many varieties of fruit, especially in lemons, in which it occurs in the free condition. It is found in currants, whortleberries, raspberries, gooseberries, etc., etc.

It is prepared from lemon juice, and also by the fermentation of glucose by *citromycetes pfefferianus* and a few other ferments. After the fermentation the mass is treated with lime. The lime salt thus obtained in the form of a precipitate, is collected, and decomposed with sulphuric acid. One hundred parts of lemons yield $5\frac{1}{2}$ parts of the acid.

Citric acid crystallizes in rhombic prisms which are very easily soluble in water. The crystallized acid melts at 100°, the anhydrous at 153° to 154°. Heated to 175° it loses water and yields aconitic acid (which see): —

$$C_3H_4(OH) \begin{cases} CO_2H \\ CO_2H \\ CO_2H \end{cases} = C_3H_3 \begin{cases} CO_2H \\ CO_2H \\ CO_2H \end{cases} + H_2O.$$

Aconitic acid.

Note for Student. — Compare with formation of acrylic from hydracrylic acid; and of maleïc and fumaric acids from malic acid.

Aconitic acid takes up hydrogen, and is transformed into tricarballylic acid (which see). Thus a clear connection between tricarballylic acid and citric acid is traced; the latter is hydroxy-tricarballylic acid. Citric acid may be made from acetone-dicarbonic acid, $\begin{matrix} CH_2 . CO_2H \\ | \\ CO \\ | \\ CH_2 . CO_2H \end{matrix}$ by treating this with hydrocyanic acid and saponifying[1] the nitril thus formed:

[1] The conversion of a nitril into the corresponding carboxyl compound is generally called saponification, though, strictly speaking, it is not the same reaction as saponification proper.

$$\begin{array}{l} CH_2 . CO_2H \\ | \\ CO \\ | \\ CH_2 . CO_2H \end{array} + HCN = \begin{array}{l} CH_2 . CO_2H \\ | \\ C{<}\begin{array}{l} OH \\ CN \end{array} \\ | \\ CH_2 . CO_2H \end{array} ;$$

$$\begin{array}{l} CH_2 . CO_2H \\ | \\ C{<}\begin{array}{l} OH \\ CN \end{array} \\ | \\ CH_2 . CO_2H \end{array} + 2\,H_2O = \begin{array}{l} CH_2 . CO_2H \\ | \\ C{<}\begin{array}{l} OH \\ CO_2H \end{array} \\ | \\ CH_2 . CO_2H \end{array} + NH_3.$$

This synthesis shows that the hydroxyl in citric acid is in combination with the central carbon atom.

When rapidly heated to a temperature above 175°, citric acid first gives aconitic acid, then loses water and forms the corresponding anhydride, which in turn loses carbon dioxide and gives *itaconic anhydride* (see itaconic acid). This latter anhydride is then partly converted into *citraconic anhydride* (see citraconic acid) by the action of heat.

Citrates. A few of the salts of citric acid are: —

Mono-potassium citrate, $KH_2 . C_6H_5O_7 + 2\,H_2O$;

Di-potassium citrate, $K_2H . C_6H_5O_7$;

Tri-potassium citrate, $K_3 . C_6H_5O_7 + H_2O$. All these potassium salts are easily soluble in water. They are made by mixing citric acid and potassium carbonate in the right proportions.

Calcium citrate, $Ca_3(C_6H_5O_7)_2 + 4\,H_2O$. This salt is formed by mixing a citrate of an alkali with calcium chloride. It is more easily soluble in cold than in hot water; hence boiling causes a precipitate in dilute solutions.

Magnesium citrate, $Mg_3(C_6H_5O_7)_2 + 14\,H_2O$. This is made by dissolving magnesia in citric acid. It is used in medicine.

Hydroxy-acids, $C_nH_{2n-2}O_8$.

It has been pointed out that the hex-acid alcohols are converted by oxidation into pentahydroxy-monobasic acids. By

further oxidation these pentahydroxy-monobasic acids are converted into tetrahydroxy-dibasic acids. Thus glucose, $CH_2OH(CHOH)_4CH_2OH$, when oxidized, yields, first, gluconic acid, $CH_2OH(CHOH)_4CO_2H$, and then *saccharic acid*, $CO_2H(CHOH)_4CO_2H$, a tetrahydroxy-dibasic acid. Corresponding to each gluconic acid there is a saccharic acid. So also the mannonic acids yield *mannosaccharic acids*, which are dibasic and isomeric with the saccharic acids; and galactonic acid yields *mucic acid*. The best known members of this group are saccharic and mucic acids.

Saccharic acid, $C_6H_{10}O_8\left(=C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — The dextro variety is formed by the oxidation of cane sugar, *d*-glucose, sugar of milk, or starch with nitric acid.

It is an amorphous mass that becomes solid only with difficulty. When treated with hydriodic acid it is reduced to adipic acid, a member of the oxalic acid series (see table, page 142): —

$$\underset{\text{Saccharic acid.}}{C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}}+8\,HI=\underset{\text{Adipic acid.}}{C_4H_8<\begin{matrix}CO_2H\\CO_2H\end{matrix}}+4\,H_2O+8\,I.$$

Mucic acid, $C_6H_{10}O_8\left(=C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — This is formed by the oxidation of sugar of milk, the gums, dulcite, or galactose with nitric acid. It is best prepared from sugar of milk.

It is a crystalline powder which is very difficultly soluble in cold water. Hydriodic acid reduces it to adipic acid (see above, under Saccharic acid).

When heated with pyridine to 140°, mucic acid is changed to the isomeric form, *allomucic acid*.

CHAPTER XI.

CARBOHYDRATES.

Among the mixed compounds are the important substances commonly known as *carbohydrates*. This name was originally given to them because they consist of carbon in combination with hydrogen and oxygen, which two elements are present in the proportion to form water, as shown in the formulas, for glucose, $C_6H_{12}O_6$, starch, $C_6H_{10}O_5$, etc. In view of recent discoveries the name is no longer accurate, as some substances belonging to this group are now known that do not contain hydrogen and oxygen in the proportion to form water. Such a substance, for example, is rhamnose, $C_6H_{12}O_5$. The name carbohydrate has, however, been used so long that it would be difficult to supplant it.

The carbohydrates may be conveniently classified under three heads. These are: —

1. *Monosaccharides* or *simple sugars.* — Examples of these are glucose, fructose, arabinose, and mannose.

2. *Polysaccharides* or *complex sugars.* — Examples are cane sugar, sugar of milk, maltose, and isomaltose.

3. *Polysaccharides, not resembling sugars.* — Examples are cellulose, starch, and gums.

The monosaccharides are the simplest carbohydrates. Those that are best known have the composition, $C_6H_{12}O_6$, and are related to the hex-acid alcohols, sorbite and mannite, $C_6H_8(OH)_6$. There are, however, simpler ones, such as arabinose, $C_5H_{10}O_5$, erythrose, $C_4H_8O_4$, and glycerose, $C_3H_6O_3$; and some that are more complex, as heptose, $C_7H_{14}O_7$, octose, $C_8H_{16}O_8$, and nonose, $C_9H_{18}O_9$. The monosaccharides, therefore, fall into classes which are called *trioses, tetroses, pentoses, hexoses*, etc., according to the number of oxygen atoms contained in them.

By methods which will be explained below, it has been shown that the monosaccharides or simple sugars are *aldehyde-alcohols* (*aldoses*) or *ketone-alcohols* (*ketoses*).

1. Monosaccharides.

A. *Trioses* and *Tetroses.*

Glycerose, $C_3H_6O_3$. — This sugar deserves special mention as being the simplest member of the group of monosaccharides, and as having been obtained artificially. It is formed by treating glycerol with mild oxidizing agents, as, for example, bromine and sodium hydroxide. It is a mixture of glyceric aldehyde and dioxyacetone, the relations of which to glycerol are shown by the following formulas: —

CH_2OH	CHO	CH_2OH
$\vert$	$\vert$	$\vert$
$CHOH$	$CHOH$	CO
$\vert$	$\vert$	$\vert$
CH_2OH	CH_2OH	CH_2OH
Glycerol.	Glyceric aldehyde.	Dioxy-acetone

Glycerose is a syrup that undergoes fermentation and reduces alkaline solutions of copper salts, acting thus like many of the sugars, as will be shown. Glyceric aldehyde is a simple example of an aldose or aldehyde-alcohol, and dioxy-acetone is the simplest example of a ketose or ketone-alcohol.

When the mixture of these two substances is treated with caustic soda it is converted into *i-acrose*, a sugar of special importance, as it forms the starting point in the synthetical operations that lead to the formation of all the members of the glucose group.

Erythrose, $C_4H_8O_4$, has been obtained from erythrite in the same way that glycerose is obtained from glycerol.

B. *Pentoses.*

Arabinoses, $C_5H_{10}O_5$. — Ordinary arabinose is obtained from cherry gum by boiling with dilute sulphuric acid. This

variety is called *levo-arabinose* on account of its relation to levo-glucose and levo-mannose, although it turns the plane of polarization to the right. *Dextro-arabinose* and inactive arabinose have also been obtained, the latter by combination of the levo and dextro varieties.

Xylose, $C_5H_{10}O_5$, is obtained from wood gum by boiling with dilute acids.

Rhamnose, $C_6H_{12}O_5$, has been obtained by the breaking down of a number of natural substances, such as quercitrin. It has been shown to be a methyl derivative of a pentose, and is therefore to be represented by the formula $CH_3.C_5H_9O_5$.

C. *Hexoses.*

Glucose, grape sugar (**dextrose**), $C_6H_{12}O_6$. — Glucose occurs very widely distributed in the vegetable kingdom, especially in sweet fruits, in which it is found together with an equivalent quantity of fructose or fruit sugar. It is also found in honey, together with fructose; and, further, in the blood, in the liver, and in the urine; and in the disease *Diabetes mellitus*, the quantity contained in the urine is largely increased, reaching as high as 8 to 10 per cent.

Glucose is formed from several of the carbohydrates of the formulas $C_{12}H_{22}O_{11}$ and $C_6H_{10}O_5$, by boiling with dilute mineral acids, or by the action of *enzymes*.[1] The formation from cane sugar takes place according to this equation, equivalent quantities of glucose and fructose being formed: —

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Starch, cellulose, and dextrin yield glucose according to this equation: —

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

[1] *Enzymes*, substances of the order of albumin, have the power to bring about important changes in some of the carbohydrates. They are called *unorganized ferments*, as they act in general like the organized ferments or ferments proper. Among the important enzymes are *diastase* and *invertin*.

Finally, glucose occurs in nature, in combination with a number of carbon compounds, in the so-called *glucosides*. These break up easily when treated with dilute mineral acids or ferments, and yield glucose as one of the products (see Glucosides). Examples of the glucosides are amygdalin, æsculin, salicin, etc.

Glucose is prepared on the large scale from corn starch in the United States, and from potato starch in Germany. The transformation is usually effected by boiling with dilute sulphuric acid. The excess of acid is removed by treating the solutions with chalk, and filtering. The filtered solutions are evaporated down either to a syrupy consistency, and sent into the market under the names "glucose," "mixing syrup," etc., or to dryness, the solid product being known in commerce as "grape sugar." By evaporating the solutions down to such a concentration that they contain from 12 to 15 per cent of glucose, crystals are formed which closely resemble those of cane sugar. They consist of anhydrous grape sugar. Their formation is facilitated by adding a little of the crystallized substance to the concentrated solutions.

If in the treatment of starch with sulphuric acid the transformation is not complete, and this is usually the case, the product is a mixture of glucose, maltose, and dextrin. The longer the action continues, the larger the percentage of glucose.

Glucose crystallizes from concentrated solutions, usually in crystalline masses consisting of minute six-sided plates. The mass, as seen in commercial "granulated grape sugar," looks very much like granulated sugar. It crystallizes from alcohol in monoclinic crystals. The sweetness of glucose is to that of cane sugar as 3 to 5. *Its solutions turn the plane of polarization to the right.*

Glucose is easily oxidized, reducing the salts of silver and copper. When treated with nascent hydrogen, it yields Sorbite (which see). Under the influence of yeast it ferments, yielding mainly alcohol and carbon dioxide. Putrid cheese transforms it first into lactic acid and then into butyric acid by the so-called lactic acid fermentation.

Glucose forms compounds with metals and salts. Among the better known compounds of this kind are those mentioned below: —

Sodium glucose . . . . $C_6H_{11}O_6 . Na$;

Sodium chloride glucose . $2\,C_6H_{12}O_6 . NaCl + H_2O$;

also $C_6H_{12}O_6 . NaCl + \frac{1}{2}\,H_2O$, and $C_6H_{12}O_6 . 2\,NaCl$. These compounds, with sodium chloride, crystallize well, and can be easily obtained in pure condition.

Cupric oxide glucose . . . $C_6H_{12}O_6 . 5\,CuO$.

By treatment with acetic anhydride, glucose yields a product containing five acetyl groups, pent-acetyl-glucose,

$$C_6H_7(C_2H_3O)_5O_6.$$

NOTE FOR STUDENT. — What does the formation of this compound indicate?

It is often important to know the quantity of glucose contained in a given liquid; as, for example, in the urine in a case of suspected diabetes. For the purpose of making the estimation, advantage is taken of the action of glucose towards an alkaline solution of copper sulphate. The solution commonly used is that known as *Fehling's solution.* It is prepared by dissolving 34.64^g crystallized pure copper sulphate in 200^{cc} water, adding a solution of 150^g potassium tartrate, and 90^g sodium hydroxide, and diluting so that the whole makes one litre.

Experiment 38. Make half the quantity of Fehling's solution above mentioned, and put in a bottle with a glass stopper. In a test-tube boil about 10^{cc} of this solution, and then add a few drops of a dilute solution of glucose. Continue to boil, and add a little more of the glucose solution; and so on, until, on removing the tube from the lamp, a dark-red uniform-looking precipitate settles, leaving the liquid above it perfectly clear and colorless. This precipitate is cuprous oxide. By taking proper precautions, the exact amount of glucose present in a solution can be estimated in this way.

Ordinary glucose is known as *d*-glucose on account of its dextro-rotatory power. Both *l*-glucose and *i*-glucose have been made.

Fructose, fruit sugar (levulose), $C_6H_{12}O_6$. — This sugar occurs together with glucose, and in equivalent quantities, in fruits; and is formed by the action of dilute mineral acids, or ferments, on cane sugar. Pure fructose is obtained by heating inulin, a carbohydrate of the formula $C_{12}H_{20}O_{10}$, with very dilute acids. It is also formed by the oxidation of *d*-mannite.

Ordinary fructose is called *d*-fructose, although it turns the plane of polarization to the left. The reason for this is that it is related to other substances that are dextro-rotatory.

Fructose can be obtained in the form of crystals. It is about as sweet as cane sugar, and has been proposed as a substitute for this in diabetes.

i-**Fructose** has been made artificially in three ways: —

1. By polymerisation of formic aldehyde, CH_2O, by means of bases;

2. By successive treatment of acroleïn with bromine and baryta water;

3. By the action of dilute alkali on glycerose, which is formed by oxidation of glycerol.

It will be observed that formic aldehyde has the same percentage composition as fructose. It is the simplest possible compound to which the name carbohydrate can be applied.

When acroleïn is treated with bromine, two atoms of the latter are added directly to the former: —

$$\begin{array}{l} CH_2 \\ | \\ CH \\ | \\ COH \end{array} + 2\,Br = \begin{array}{l} CH_2Br \\ | \\ CHBr. \\ | \\ COH \end{array}$$

When this dibromide is treated with baryta water, hydroxyl is first substituted for bromine, and glyceric aldehyde is the first product. This then is polymerised and forms *i*-fructose: —

$$\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ COH \end{array} + Ba(OH)_2 = \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COH \end{array} + BaBr_2;$$

$$2\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COH \end{array} = C_6H_{12}O_6.$$

On account of the formation of *i*-fructose from acrolein it was called *acrose*. It was later shown to be the inactive variety of fructose, and the name acrose became unnecessary, though it is still used.

The formation of *i*-fructose from glycerose takes place as represented in the following equation: —

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHO \end{array} + \begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ CH_2OH \end{array} = CH_2OH - CHOH - CHOH - CHOH - CO - CH_2OH.$$

The aldehyde group CHO reacts with one of the CH_2OH groups of the ketone thus: —

$$\begin{array}{llll} H & H & H & H \\ C=O & + CHOH & = C - OH & - COH. \end{array}$$

This reaction is known as the *aldol condensation*, because the product first obtained in this way was called *aldol*. This was formed by condensation of ordinary aldehyde thus: —

$$CH_3.CHO + CH_3.CHO = \underset{\text{Aldol.}}{CH_3.CHOH.CH_2.CHO}.$$

Aldol is really β-hydroxybutyric aldehyde.

When *i*-fructose is treated with yeast, it is partly transformed by the ferment into alcohol and carbon dioxide. It is the *d*-fructose contained in it that undergoes the change, while the *l*-fructose remains behind unchanged, and can be obtained free from the other two varieties.

Constitution of glucose and fructose. — Two reactions have been of special value in the determination of the constitution of the members of the group of monosaccharides.

a. When either an aldehyde or an acetone is treated with hydrocyanic acid an addition-product is formed thus: —

$$CH_3.\overset{H}{\overset{|}{C}}=O+HCN=CH_3.\overset{H}{\overset{|}{C}}<\begin{matrix}OH\\CN\end{matrix};$$

and

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C=O+HCN=\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OH\\CN\end{matrix}.$$

The products can be converted into corresponding acids by the change of the cyanogen group into carboxyl. Thus the nitril from aldehyde yields *a*-hydroxypropionic (or lactic) acid: —

$$CH_3.\overset{H}{\overset{|}{C}}<\begin{matrix}OH\\CN\end{matrix}+2\,H_2O=CH_3.\overset{H}{\overset{|}{C}}<\begin{matrix}OH\\COOH\end{matrix}+NH_3;$$

while the nitril from acetone yields *a*-hydroxyisobutyric acid: —

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OH\\CN\end{matrix}+2\,H_2O=\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OH\\COOH\end{matrix}+NH_3.$$

By the aid of these reactions it has been shown that glucose is an aldose, and fructose a ketose, of these formulas: —

(1) $CHO-CHOH-CHOH-CHOH-CHOH-CH_2OH.$
Glucose.

(2) $CH_2OH-CO-CHOH-CHOH-CHOH-CH_2OH.$
Fructose.

By adding hydrocyanic acid to a compound of formula (1) a nitril of the following formula would be formed: —

$$\begin{matrix}CN\\HO\end{matrix}>CH-CHOH-CHOH-CHOH-CHOH-CH_2OH.$$

This would yield an acid of the formula: —

$$\begin{matrix}HOOC\\HO\end{matrix}>CH-CHOH-CHOH-CHOH-CHOH-CH_2OH.$$

By treating this with hydriodic acid it would be reduced to the acid: —

$$HO_2C.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3.$$

The acid obtained from dextrose by means of the above reactions has the structure represented by this formula, and it hence follows that dextrose itself must have the structure represented by formula (1) above, or it must be an aldose.

By subjecting fructose to the same processes, the product obtained has the structure: —

$$\begin{array}{l} \quad\quad CO_2H \\ \quad\quad | \\ CH_3.CH.CH_2.CH_2.CH_2.CH_3; \end{array}$$

and it follows from this that fructose must have the structure represented by formula (2) above, or it must be a ketose.

b. When an aldehyde or an acetone is treated with phenylhydrazine, $C_6H_5.NH.NH_2$, a reaction takes place, as represented in this equation: —

$$\begin{array}{l} \quad H \quad\quad\quad\quad\quad\quad\quad\quad\quad H \\ \quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad | \\ R.C=O + H_2N.NHC_6H_5 = R.C=N.NHC_6H_5 + H_2O. \end{array}$$

The products thus formed are called *hydrazones*.

The sugars form hydrazones when treated with phenylhydrazine. Thus dextrose and fructose give the products

(1) $CH_2OH.CHOH.CHOH.CHOH.CHOH.CH$
$\quad\quad\quad\quad\quad\quad\quad\quad

phenylhydrazine is combined, is oxidized to the ketone group CO and then phenylhydrazine reacts with this in the usual way, the product being a compound of the formula —

$$CH_2OH - CHOH - CHOH - CHOH - \underset{\|}{C} - \underset{\|}{CH}$$
$$C_6H_5HN.N \quad N.NHC_6H_5.$$

This is called an **osazone** or, specifically, **glucosazone.**

In the case of fructose, the primary alcohol group, CH_2OH, adjoining the carbon atom with which the residue of phenylhydrazine is combined is oxidized to the aldehyde group, CHO, and then phenylhydrazine reacts with this in the usual way, giving a product of the formula —

$$CH_2OH.CHOH.CHOH.CHOH.\underset{\|}{C}.\underset{\|}{CH}$$
$$C_6H_5HN.N \quad N.NHC_6H_5.$$

This is the osazone of fructose or **fructosazone.** Glucosazone and fructosazone are identical.

The osazones are in general difficultly soluble in water and have characteristic properties whereby they can be recognized. The sugars themselves are easily soluble and it is hard to separate them, and until the discovery of the phenylhydrazine reaction the investigation of the sugars advanced very slowly. This reaction in the hands of one of the most skilful experimenters has advanced our knowledge of the sugar group enormously within a few years past.

The formation of the osazones makes it possible to recognize the different sugars, but it does not give the sugars themselves. The regeneration of the sugars from the osazones is of great importance. The principal reactions available for this purpose are the following: —

1. The osazone is heated for a short time with fuming hydrochloric acid when it yields phenylhydrazine hydrochloride and an *osone,* thus: —

$$\begin{array}{c} CH_2OH\,.\,(CHOH)_3\,.\,C\,.\,C + 2\,H_2O + 2\,HCl \\ \qquad\qquad\quad \| \quad \| \\ \qquad\qquad\quad C_6H_5HN\,.\,N \quad N\,.\,NHC_6H_5 \end{array}$$

$$= \underset{\text{Osone.}}{CH_2OH(CHOH)_3CO\,.\,CHO} + 2\,C_6H_5\,.\,NH\,.\,NH_2\,.\,HCl.$$

2. The osone can be isolated and reduced by means of acetic acid and zinc dust, when it is converted into the corresponding ketose: —

$$CH_2OH(CHOH)_3CO\,.\,CHO + 2\,H$$
$$= CH_2OH(CHOH)_3\,.\,CO\,.\,CH_2OH.$$

Whether the original sugar was an aldose or a ketose, the final product of the above series of reactions is a ketose. The aldoses cannot, therefore, be regenerated in this way. On the other hand, any aldose can be converted into a ketose by this means.

Mannose, $C_6H_{12}O_6$. — *d*-Mannose is one of the products of oxidation of *d*-mannite, and is obtained by the action of dilute acids on some kinds of cellulose. The shavings formed in the manufacture of buttons from vegetable ivory are rich in the cellulose which yields *d*-mannose.

***l*-Mannose** and ***i*-mannose** have also been prepared.

The mannoses are aldehydes, and are stereoisomeric with glucose.

Galactose, $C_6H_{12}O_6$. — *d*-Galactose is formed by treatment of sugar of milk with dilute acids, *d*-glucose being formed at the same time. Other carbohydrates also yield it. *l*- and *i*-Galactoses are known. By reduction *d*- and *l*-galactoses are transformed into dulcite. By oxidation all three galactoses yield mucic acid.

Gulose, $C_6H_{12}O_6$. — The three guloses have been made artificially. They are aldoses corresponding to the three sorbites, and are stereoisomeric with the glucoses.

The method by which *l*-gulose was made is of special interest, as it is based upon reactions that may be used for passing from

an aldose of a certain composition to one containing one carbon atom more. This method, as will be seen, makes it possible to pass from a pentose to a hexose, from a hexose to a heptose, etc. It consists in adding hydrocyanic acid to the aldose, converting the nitril thus obtained into the corresponding acid, and then reducing the acid. Thus in the case of *l*-gulose the starting-point is xylose, and the steps may be briefly represented thus: —

Xylose → (addition of hydrocyanic acid) → *l*-gulonic acid → reduction → *l*-gulose.

2. Polysaccharides or Complex Sugars.

The polysaccharides, or complex sugars, are found in nature, as, for example, cane sugar and sugar of milk, or are formed from more complex carbohydrates, as, for example, maltose from starch. Their most characteristic property is their power to break down into monosaccharides under the influence of dilute acids or enzymes. The reaction involves the addition of the elements of water, and is called *hydrolysis.* A simple example of this kind of action is the conversion of maltose into *d*-glucose: —

$$\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = 2\,\underset{d\text{-Glucose.}}{C_6H_{12}O_6}.$$

In most cases the hydrolysis of a polysaccharide gives more than one monosaccharide. Cane sugar, for example, gives *d*-glucose and *d*-fructose: —

$$\underset{\text{Cane Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{d\text{-Glucose.}}{C_6H_{12}O_6} + \underset{d\text{-Fructose.}}{C_6H_{12}O_6};$$

sugar of milk gives *d*-galactose and *d*-glucose: —

$$C_{12}H_{22}O_{11} + H_2O = \underset{d\text{-Galactose.}}{C_6H_{12}O_6} + \underset{d\text{-Glucose.}}{C_6H_{12}O_6}.$$

Polysaccharides that give two monosaccharides when hydrolyzed are known as *saccharobioses;* those that give three, as *saccharotrioses.*

Cane sugar, Saccharose, $C_{12}H_{22}O_{11}$. — This well-known variety of sugar occurs very widely distributed in nature, in sugar cane, sorghum, the Java palm, the sugar maple, beets, madder root, coffee, walnuts, hazel nuts, sweet and bitter almonds; in the blossoms of many plants; in honey, etc., etc.

It is obtained mainly from the sugar cane and from beets. In either case the processes of extraction and refining are largely mechanical. When sugar cane is used, this is macerated with water to dissolve the sugar. Thus a dark-colored solution is obtained. This is evaporated, and then passed through filters of bone-black which remove the coloring matter. The solution is evaporated in the air to some extent, and then in large vessels called "vacuum pans," from which the air is partly exhausted, so that the boiling takes place at a lower temperature than would be required under the ordinary pressure of the atmosphere. The mixture of crystals and mother liquors obtained from the "vacuum pans" is freed from the liquid by being brought into the "centrifugals." These are funnel-shaped sieves which are revolved very rapidly, the liquid being thus thrown by centrifugal force through the openings of the sieve, while the crystals remain behind and are thus nearly dried. The final drying is effected by placing the crystals in a warm room.

When beets are used, the process is essentially the same, though there are some differences in the details.

The mother liquors which are obtained from the "centrifugals" are further evaporated, and yield lower grades of sugar; and, finally, a syrup is obtained which does not crystallize. This is *molasses*. Molasses is sometimes brought into the market as such; sometimes, particularly when obtained from beet sugar, it is allowed to ferment for the purpose of making alcohol. The spent wash, or waste liquor, "vinasse," is now evaporated to dryness and calcined for the purpose of getting the alkaline salts contained in the residues. The products of distillation are collected, and from them tri-methyl-amine is separated (see p. 96).

Sugar crystallizes from water in well-formed, large monoclinic prisms. It is dextro-rotatory. When heated to 210° to 220°, cane sugar loses water, and is converted into the substance called *caramel*, which is more or less brown in color, according to the duration of the heating and the temperature reached. Boiled with dilute mineral acids, cane sugar is split into equal parts of glucose and fructose, as has been stated. The mixture of the two is called *invert-sugar*. The process is called *inversion*. It takes place, to some extent, when impure sugar is allowed to stand. Hence invert-sugar is contained in the brown sugars found in the market. The enzyme, invertin (see p. 184), formed by yeast, gradually transforms cane sugar into glucose and fructose, and these then undergo fermentation. Cane sugar itself does not ferment.

Cane sugar does not reduce an alkaline solution of copper sulphate. If the two are boiled together for some time, the sugar is to some extent inverted, and to this extent reduction of the copper salt takes place.

Experiment 39. Prepare a dilute solution of cane sugar by dissolving 1^{g} to 2^{g} in 200^{cc} water. Test this with Fehling's solution, as in Exp. 38. Now add to the sugar solution 10 drops concentrated hydrochloric acid, and heat for half an hour on the water-bath at 100°; exactly neutralize the acid with a dilute solution of sodium carbonate, and test with Fehling's solution.

Oxidizing agents readily convert cane sugar into oxalic acid (see Exp. 34) and saccharic acid.

Like glucose, cane sugar forms compounds with metals, metallic oxides, and salts. Among these the following may be mentioned: —

Sodium sucrate . . . . $C_{12}H_{21}O_{11}.Na$,

Sodium-chloride sucrate . . $C_{12}H_{22}O_{11}.NaCl$,

Calcium sucrate . . . . $C_{12}H_{20}O_{11}.Ca$,

and *Lime sucrate* . . . . . $C_{12}H_{22}O_{11}.2\,CaO$.

These derivatives are not sweet.

An *oct-acetate* of the formula $C_{12}H_{14}(C_2H_3O)_8O_{11}$ has been made by treating sugar with sodium acetate and acetic anhydride.

Cane sugar is in some way made up by a combination of a molecule of *d*-glucose and a molecule of *d*-fructose, with elimination of a molecule of water. The resulting compound does not react with phenylhydrazine nor with Fehling's solution, and, therefore, it probably does not contain a carbonyl group CO. The artificial preparation of cane sugar from *d*-glucose and *d*-fructose has not been effected.

Sugar of milk, lactose, $C_{12}H_{22}O_{11} + H_2O$. — This sugar occurs in the milk of all mammals, and is obtained in the manufacture of cheese. The caseïn is separated from the milk by means of rennet; the sugar of milk remains in solution, is separated by evaporation, and purified by recrystallization. It crystallizes in rhombic crystals. That which comes into the market has been crystallized on strings or wood splinters. It has a slightly sweet taste; is much less soluble in water than cane sugar, and is dextro-rotatory. It reduces Fehling's solution. Oxidized with nitric acid, it yields mucic and saccharic acids. Nascent hydrogen converts sugar of milk into mannite, dulcite, and other substances. Like glucose and cane sugar, it forms compounds with bases, dissolving lime, baryta, lead oxide, etc.

Sugar of milk ferments under certain circumstances, and is thus converted into lactic acid. The souring of milk is a result of this fermentation. The lactic acid formed coagulates the caseïn; hence the thickening.

Maltose, $C_{12}H_{22}O_{11}$. — This carbohydrate is formed by the action of *malt* on starch. Malt, which is made by steeping barley in water until it germinates, and then drying it, contains a substance called *diastase*, which has the power of effecting changes similar to some of those effected by the ferments. Thus, it acts upon starch, and converts it into dextrin and maltose: —

$$3\,C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11} + C_6H_{10}O_5.$$
Starch. Maltose. Dextrin.

Maltose is also formed by the action of dilute sulphuric acid upon starch, and is hence contained in commercial glucoses. By further treatment with sulphuric acid it is converted into glucose. Maltose crystallizes in fine needles; is dextro-rotatory; reduces Fehling's solution, and ferments with yeast, it being first converted into monosaccharides by *maltase*, which is an enzyme contained in, or formed by, yeast.

3. Polysaccharides, not Resembling Sugars.

Cellulose, $(C_6H_{10}O_5)_x$. — Cellulose forms the groundwork of all vegetable tissues. It presents different appearances and different properties, according to the source from which it is obtained; but these differences are due to substances with which the cellulose is mixed; and when they are removed, the cellulose left behind is the same thing, no matter what its source may have been. The coarse wood of trees, as well as the tender shoots of the most delicate plants, all contain cellulose as an essential constituent. It forms the membrane of the cells. Cotton-wool, hemp, and flax consist almost wholly of cellulose.

For the preparation of cellulose, either Swedish filter-paper or cotton-wool may be taken.

Experiment 40. Treat some cotton-wool successively with ether, alcohol, water, a caustic alkali, and, finally, a dilute acid. Then wash with water.

Cellulose is amorphous; insoluble in all ordinary solvents; soluble in an ammoniacal solution of cupric oxide. It dissolves in concentrated sulphuric acid. If the solution is diluted and boiled, the cellulose is converted into dextrin and glucose. It will thus be seen that rags, paper, and wood, which consist largely of cellulose, might be used for the preparation of glucose, and consequently of alcohol.

Experiment 41. Dissolve a sheet or two of filter-paper in as small a quantity of concentrated sulphuric acid as will suffice ; dilute with water to about half to three-quarters of a litre, and boil for an hour. Remove the sulphuric acid by means of chalk ; filter ; evaporate ; and test for glucose by means of Fehling's solution.

Gun cotton, pyroxylin, nitro-cellulose. — Cellulose has some of the properties of alcohols; among them the power to form ethereal salts with acids. Thus, when treated with nitric acid, it forms several nitrates, just as glycerol forms the nitrates known as nitro-glycerin (which see).

When cotton is exposed for some time to the action of a warm mixture of nitre and sulphuric acid, *soluble cotton* or *soluble pyroxylin* is formed. This consists of the lower nitrates (the di-, tri-, and tetra-nitrates), which are soluble in ether containing a little alcohol.

The solution is called *collodion solution.* When poured upon the surface of a solid, such as glass, the ether and alcohol rapidly evaporate and leave a thin coating of the nitrates. It finds extensive application in surgery and in photography.

When treated with a mixture of nitric and sulphuric acids, cotton yields the higher nitrates (tetra-, penta-, and hexa-nitrates). These are called *gun cotton* or *pyroxylin.* They are extensively used as explosives. Gun cotton forms the active constituent of some of the *smokeless powders* now so extensively used. In the manufacture of these powders the gun cotton is gelatinized by treating it, in finely divided condition, with acetone or some other similar solvent. Under these circumstances the gun cotton does not dissolve, but it swells up and forms a gelatinous mass. From this the solvent is removed by pressure and evaporation, and the residual mass cut into laminæ, or powdered by appropriate methods. The name "explosive gelatin" is given to the substance prepared as above.

A solution of soluble cotton in molten camphor gives *celluloid.* As it is plastic at a slightly elevated temperature, it can easily be moulded into any desired shape. When it cools it hardens.

Paper. — Paper in its many forms consists mainly of cellulose. The essential features in the manufacture of paper are, first, the disintegration of the substances used. This is effected partly mechanically, and partly by boiling with caustic soda. The mass is converted into pulp by means of knives placed on rollers. The pulp, with the necessary quantity of water, is then passed between rollers. Chiefly rags of cotton or linen are used in the manufacture of paper; wood and straw are also used.

Starch, $(C_6H_{10}O_5)_x$. — Starch is found everywhere in the vegetable kingdom in large quantity, particularly in all kinds of grain, as maize, wheat, etc.; in tubers, as the potato, arrowroot, etc.; in fruits, as chestnuts, acorns, etc.

In the United States starch is manufactured mainly from maize; in Europe, from potatoes.

The processes involved in the manufacture of starch are mostly mechanical. The maize is first treated with warm water; the softened grain is then ground between stones, a stream of water running continuously into the mill. The thin milky fluid which is carried away is brought upon sieves of silk bolting-cloth, which are kept in constant motion. The starch passes through with the water as a milky fluid, and this is allowed to settle when the water is drawn off. The starch is next treated with water containing a little alkali (caustic soda, or sodium carbonate), the object of which is to dissolve gluten, oil, etc. The mixture is now brought into shallow, long wooden runs, where the starch is deposited, the alkaline water running off. Finally, the starch is washed with water, and dried at a low temperature.

Starch has a granular structure, the grains as seen under the microscope having a series of concentric markings, the nucleus of which is at one side.

Starch in its usual condition is insoluble in water. If ground with cold water, it is partly dissolved. If heated with water, the membranes of the starch-cells are broken, and the contents

form a partial solution. On cooling, it forms a jelly called *starch paste.*

With iodine, starch paste gives a deep blue color; with bromine, a yellow color.

Experiment 42. Make some starch paste thus: Put a few grams of starch[1] in an evaporating dish; pour enough cold water upon it to cover it; grind it under the water with a pestle, and then pour 200cc to 300cc hot water upon it. When this is cool, add a few drops to a litre of water, and then add a few drops of potassium iodide. As long as the iodine is in combination with the potassium no change of color takes place; but if the iodine is set free by the addition of a drop or two of chlorine water, or of strong nitric acid, the entire liquid turns a beautiful dark blue. The cause of this color is the formation of a very unstable compound of starch and iodine. The color is easily destroyed by a slight excess of chlorine water (try it in a test-tube); by alkalies (try it); by sulphurous acid (try it); by hydrogen sulphide (try it); etc. It is also destroyed by heating. (Heat some of the solution in a test-tube, and let it stand.) The color reappears on cooling.

Experiment 43. Use some of the starch paste in studying the effect of bromine upon it. Use dilute solutions. The bromine must be in the free condition.

Starch is converted into dextrin, maltose, and glucose by dilute acids; diastase converts it into maltose and dextrin.

Experiment 44. Add 20cc concentrated hydrochloric acid to 200cc of the starch paste already made, and heat for two hours on the water-bath, connecting the flask with an inverted condenser (see Fig. 8). Then examine with Fehling's solution. Test, also, some of the original starch paste with Fehling's solution.

When starch is treated for a few days with cold, dilute mineral acids, it is converted into "soluble starch," which dissolves in water without the formation of a paste.

Glycogen, $(C_6H_{10}O_5)_x$. This is a carbohydrate resembling starch that occurs in the animal organism. It is found in

[1] The purest form of starch to be found in the market is that made from arrow-root. Ordinary starch contains other substances which sometimes interfere with the reactions.

the muscles, but disappears during exercise or hunger. It is especially abundant in the liver of healthy animals. It yields dextrin, maltose, and *d*-glucose when hydrolysed.

Dextrin, $C_6H_{10}O_5$. — Dextrin is formed by treating starch with dilute acids or diastase. It is converted by further treatment with acids into glucose. The substance ordinarily called dextrin has been shown to be a mixture of several isomeric substances which resemble each other very closely. The mixture is an uncrystallizable solid. It is strongly dextro-rotatory; gives a red color with iodine, and does not reduce Fehling's solution. It is used extensively as a substitute for gum.

Gums. — Under this head are included a number of substances which occur in nature. One of the best known is *gum arabic*, which is obtained in Senegambia from the bark of trees belonging to the *Acacia* variety. Its formula, like that of cane sugar, is $C_{12}H_{22}O_{11}$. Other gums are *wood gum*, obtained from the birch, ash, beech, etc.; *bassorin*, the chief constituent of gum tragacanth, etc.

Our knowledge of the chemistry of these gums is very limited.

CHAPTER XII.

MIXED COMPOUNDS CONTAINING NITROGEN.

In speaking of the preparation of dibasic acids from monobasic acids, reference was made to cyan-acetic and the two cyan-propionic acids. These are nothing but simple cyanogen substitution-products analogous to chlor-acetic and the two chlor-propionic acids. They are made by treating the chlorine products with potassium cyanide. They have been useful chiefly in the preparation of dibasic acids, as described in connection with malonic and the two succinic acids. It will therefore not be necessary to consider them individually here.

Note for Student. — How can malonic be made from acetic acid; and the two succinic acids from propionic acid? Give the equations.

The chief substances to be considered under the head of *mixed compounds containing nitrogen* are the *amino-acids* and the *acid amides*. As will be seen, both these classes of substances are of special interest, as they represent forms of combination which are favorite ones in nature, especially in the animal kingdom, some of the most important substances found in the animal body, such as urea, uric acid, glycocoll, etc., belonging to one or both the classes.

Amino-acids.

The relation of an amino-acid to the simple acid is, as the name implies, the same as that of an amino derivative of a hydrocarbon to the hydrocarbon. That is to say, it may be regarded as the acid in which a hydrogen is replaced by the amino group, NH_2. Thus, amino-acetic acid is represented

by the formula $CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix}$; while amino-methane, or methyl-amine is represented thus, $CH_3.NH_2$. The reasons for regarding methyl-amine as a substituted ammonia, as represented, have been stated. The formula is based upon the reactions of the substance; that is, upon its chemical conduct and the methods used in its preparation. The same arguments lead in the same way to the view that the amino-acids are substituted ammonias, and, at the same time, acids. The simplest method for their preparation consists in treating halogen derivatives of the acids with ammonia; thus amino-acetic acid can be made by treating brom-acetic acid with ammonia: —

$$CH_2<\begin{matrix}Br\\CO_2H\end{matrix}+2\,NH_3=CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix}+NH_4Br.$$

Note for Student. — Compare this reaction with that made use of for making methyl-amine.

Amino-formic acid, carbamic acid, $\begin{matrix}NH_2\\|\\CO.H\end{matrix}$. — This acid is not known in the free condition. Its ammonium salt, $\begin{matrix}NH_2\\|\\CO_2NH_4\end{matrix}$, is formed when carbon dioxide and ammonia are brought together, and it is therefore contained in commercial ammonium carbonate: —

$$CO_2+2\,NH_3=\begin{matrix}NH_2\\|\\CO_2NH_4.\end{matrix}$$

The other carbamates are prepared from the ammonium salt. They are decomposed, yielding carbonates and ammonia. Thus, when potassium carbamate is warmed in water solution, decomposition takes place, as represented in the equation, —

$$NH_2.CO_2K+H_2O=NH_3+HKCO_3.$$

The *ethereal salts* of carbamic acid, called *urethanes*, are

readily made by treating the ethereal salts of chlor-formic acid (see p. 157) with ammonia: —

$$\begin{array}{l} Cl \\ | \\ CO_2C_2H_5 \end{array} + 2\,NH_3 = \begin{array}{l} NH_2 \\ | \\ CO_2C_2H_5 \end{array} + NH_4Cl.$$

Amino-formic acid cannot be taken as a fair representative of the amino-acids, any more than carbonic acid can be taken as a fair representative of the hydroxy-acids.

Glycocoll, glycine, amino-acetic acid, $C_2H_5NO_2\left(=CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix}\right)$. — In the bile are contained two complicated acids, which are known as glycocholic and taurocholic acids. When glycocholic acid is boiled with hydrochloric acid, it breaks up, yielding cholic acid and glycocoll. In the urine of horses is found an acid known as hippuric acid. When this is boiled with hydrochloric acid, it breaks up into benzoic acid and glycocoll.

When uric acid is treated with hydriodic acid, glycocoll is one of the products. Further, glycocoll is formed when glue is boiled with baryta water or dilute sulphuric acid. Its formation from brom-acetic acid and ammonia, mentioned above, gives the clearest indication in regard to its relation to acetic acid.

Amino-acetic acid is soluble in water, insoluble in alcohol or ether. It has a sweetish taste, and is sometimes called *gelatin sugar.*

Amino-acetic acid has both acid and basic properties. It unites with acids, forming weak salts; and it acts upon bases, giving salts with metals, — the amino-acetates. It also unites with salts, forming double compounds.

Examples of the compounds with acids are the

Hydrochloride . . . . $CH_2<\begin{matrix}NH_2.HCl\\CO_2H\end{matrix}$,

and the *Nitrate* . . . . . $CH_2<\begin{matrix}NH_2.HNO_3\\CO_2H\end{matrix}$;

of the salts with metals,

Zinc amino-acetate . . $Zn(C_2H_4NO_2)_2 + H_2O$,

and *Copper amino-acetate* . $Cu(C_2H_4NO_2)_2 + H_2O$;

of the compounds with salts, the double salt of

Copper nitrate and *Copper amino-acetate*, $Cu(NO_3)_2.Cu(C_2H_4NO_2)_2 + 2\,H_2O$.

Treated with nitrous acid, glycocoll is converted into hydroxy-acetic acid. With soda-lime it gives methylamine.

NOTE FOR STUDENT. — Write the equation representing the reaction which takes place when glycocoll is treated with nitrous acid.

It seems probable that amino-acetic acid and other similar compounds are really salts formed by the union of the acid constituent, carboxyl, with the basic constituent, NH_2. In accordance with this view the formula should be written thus: —

$$CH_2<\begin{matrix}NH_2\\COOH\end{matrix}> \text{ or } CH_2<\begin{matrix}NH_3\\CO\end{matrix}>O.$$

Sarcosine, methyl-glycocoll, $C_3H_7NO_2$ $\left(=CH_2<\begin{matrix}NH.CH_3,\\CO_2H\end{matrix}\right.$ or $CH_2<\begin{matrix}NH_2.CH_3\\ \\CO\end{matrix}>O\Big)$. — When brom-acetic acid is treated with methyl-amine instead of with ammonia, a reaction takes place similar to that which takes place with ammonia, the product being *methyl-glycocoll* or *sarcosine*: —

$$CH_2<\begin{matrix}Br\\CO_2H\end{matrix} + 2\,CH_3.NH_2 = CH_2<\begin{matrix}NH.CH_3\\CO_2H\end{matrix} + NH_3(CH_3)Br.$$

Sarcosine.

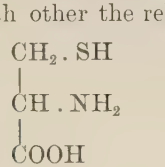
Sarcosine is a product of the decomposition of creatine, which is found in flesh, and of caffeine, which is a constituent of coffee and tea. It is obtained from creatine and caffeine by boiling them with baryta water. Its properties are much like those of glycocoll.

Amino-propionic acids, $C_3H_7NO_2$. — These acids bear to propionic acid relations similar to that which amino-acetic acid

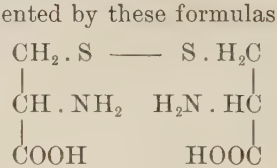
bears to acetic acid. There are two, corresponding to α- and β-chlor-propionic acids, from which they are made. They are not found in nature. Their properties are much like those of glycocoll. α-Amino-propionic acid is also called *alanin*.

NOTE FOR STUDENT. — What substances would be formed by treating the two amino-propionic acids with nitrous acids?

Cystine, $C_6H_{12}N_2O_4S_2$, a substance that is sometimes found as a crystalline sediment in the urine of human beings and dogs, is a derivative of α-amino-propionic acid. Tin and hydrochloric acid reduce it to *cysteïn*, $C_3H_7NO_2S$. The two substances bear to each other the relation represented by these formulas: —



Cysteïn.



Cystine.

Among the amino derivatives of the higher members of the fatty acid series, that of caproic acid should be specially mentioned.

Leucine, $C_5H_{10}<\begin{matrix}NH_2\\CO\end{matrix}>O$, is a substance that is found widely distributed in small quantities in the animal organism in the glands and also in the sprouts of plants. It is also formed by the decomposition of albumins and gelatin. It is probable that there are different leucines. Artificially prepared *α-amino-caproic acid*, $CH_3 . CH_2 . CH_2 . CH_2 . CH(NH_2) . CO_2H$, appears to be identical with the leucine obtained from caseïn; while that obtained from vegetable albumin, from glue and horn, is *α-amino-isobutylacetic acid*, $(CH_3)_2CH . CH_2 . CH(NH_2) . CO_2H$. Leucine is evidently of great physiological importance.

AMINO-SULPHONIC ACIDS.

Just as there are amino derivatives of the carboxyl acids, so, too, there are amino derivatives of the sulphonic acids. The most important of these is

Taurine,
β-Amino-ethyl-sulphonic acid, $C_2H_7NSO_3 \left(= C_2H_4 < \begin{matrix} SO_3H \\ NH_2 \end{matrix} \right)$.

Taurine is found in combination with cholic acid in taurocholic acid, in ox bile, and the bile of many animals, as well as in other animal liquids. It has been made synthetically from isethionic acid, $C_2H_4 < \begin{matrix} OH \\ SO_3H \end{matrix}$, by treating the acid successively with phosphorus pentachloride and ammonia: —

$$C_2H_4 < \begin{matrix} OH \\ SO_2OH \end{matrix} + 2\,PCl_5 = C_2H_4 < \begin{matrix} Cl \\ SO_2Cl \end{matrix} + 2\,POCl_3 + 2\,HCl;$$

Isethionic acid. Chlor-ethyl-sulphon-chloride.

$$C_2H_4 < \begin{matrix} Cl \\ SO_2Cl \end{matrix} + H_2O = C_2H_4 < \begin{matrix} Cl \\ SO_2OH \end{matrix} + HCl;$$

Chlor-ethyl-sulphonic acid.

$$C_2H_4 < \begin{matrix} Cl \\ SO_2OH \end{matrix} + 2\,NH_3 = C_2H_4 < \begin{matrix} NH_2 \\ SO_3H \end{matrix} + NH_4Cl.$$

Taurine.

Taurine crystallizes in large monoclinic prisms. It is a very stable substance, and can be boiled with concentrated acids without decomposition. With nitrous acids it yields isethionic acid.

It unites with strong bases forming salts, but not with acids. This conduct is in accordance with the view that taurine is an ammonium salt as represented by the formula, $C_2H_4 < \begin{matrix} NH_3 \\ SO_2 \end{matrix} > O$.

Amino-dibasic Acids.

Aspartic acid,
Amino-succinic acid, $C_4H_7NO_4 \left(= C_2H_3(NH_2) < \begin{matrix} CO_2H \\ CO_2H \end{matrix} \right)$

or $\begin{matrix} CH(NH_2) \cdot CO_2H \\ | \\ CH_2 \cdot CO_2H. \end{matrix}$

Aspartic acid occurs in pumpkin seeds, and is frequently met with as a product of boiling various natural compounds with dilute acids. Thus, for example, it is formed when caseïn and albumin are treated in this way. It is formed also when asparagine (which see) is boiled with acids or alkalies.

Aspartic acid crystallizes in rhombic prisms, which are difficultly soluble in water. The solution of the natural product is levo-rotatory. It contains an asymmetric carbon atom, and the three varieties (*d*-, *l*-, and *i*-) suggested by the theory are known. When each of the varieties is treated with nitrous acid it is converted into the corresponding malic acid.

Acid Amides.

When the ammonium salt of acetic acid is heated, it gives off water, and a body distils over which is known as *acetamide*. The reaction is represented by the following equation: —

$$CH_3 . COONH_4 = CH_3 . CONH_2 + H_2O.$$

The substance obtained has neither acid nor basic properties. An examination of the ammonium salts of other acids that contain carboxyl shows that the reaction is a general one, and a class of neutral bodies, known as the *acid amides*, can thus be obtained. As no one of the acid amides of the fatty acid series is of special importance, a few words of a general character in regard to the class will suffice.

Besides the reaction above given, there are two others of general application for the preparation of the acid amides. One consists in treating an ethereal salt of an acid with ammonia; thus, when ethyl acetate is treated with ammonia, this reaction takes place: —

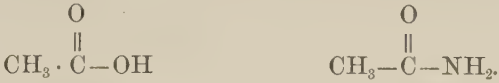
$$CH_3 . CO_2C_2H_5 + NH_3 = CH_3 . CONH_2 + C_2H_6O.$$

The other reaction consists in treating the acid chlorides with ammonia. Thus, to get acetamide, we may treat acetyl chloride (see p. 61) with ammonia: —

$$CH_3 . COCl + 2\,NH_3 = CH_3 . CONH_2 + NH_4Cl.$$

This last reaction is perhaps most frequently used. It shows the relation that exists between acetic acid and acetamide. For acetyl chloride is made from acetic acid by treatment with

phosphorus trichloride, and is, therefore, as has been pointed out, to be regarded as acetic acid in which the hydroxyl is replaced by chlorine. Now, by treatment with ammonia the same reaction takes place as that which we have had to deal with in the preparation of amino-acids; the chlorine is replaced by the amino group. Therefore, acetamide is acetic acid in which the hydroxyl is replaced by the amino group, as shown in the formulas: —



Acetic acid. Acetamide.

As the acid hydrogen of the acid is replaced, the amide is not an acid. On the other hand, the basic properties of the ammonia are destroyed by the presence of the acid residue as a part of its composition. This latter fact may be stated in another way; viz., when an ammonia residue is in combination with carbon, which in turn is in combination with oxygen, its basic properties are destroyed.

The amides are converted into ammonia and a salt when boiled with strong bases: —

$$CH_3 \cdot CONH_2 + KOH = CH_3CO_2K + NH_3.$$

They are converted into cyanides by treatment with phosphorus pentoxide, P_2O_5: —

$$CH_3 \cdot CONH_2 = CH_3 \cdot CN + H_2O.$$

As the substance obtained in this way is identical with methyl cyanide, which is formed by treating methyl-sulphuric acid with potassium cyanide, the reaction furnishes additional evidence in favor of the conclusion already reached; viz., that in the cyanides the carbon and not the nitrogen of the cyanogen group is in combination with the hydrocarbon residue, as represented in the formula CH_3-C-N.

As the amide can be made from the ammonium salt and the cyanide or nitril from the amide, so, by starting with the

cyanide, the amide and the ammonium salt can be made. The reaction by which the cyanides are converted into acids is based upon these relations. We have: —

$$R.COONH_4 \rightarrow R.CONH_2 \rightarrow R.CN,$$
$$\text{and } R \cdot CN \rightarrow R.CONH_2 \rightarrow R.COONH_4.$$

As acetamide is made by treating ammonia with the chloride of acetic acid, so, by treating ammonia with the chloride of any acid, the corresponding amide can be made. So, also, by treating ammonia with acid chlorides, or by treating acid amides with strong acids, more complicated compounds can be obtained. Of these *di-acetamide*, $NH\begin{cases} C_2H_3O \\ C_2H_3O \end{cases}$, and *tri-acetamide*, $N\begin{cases} C_2H_3O \\ C_2H_3O \\ C_2H_3O \end{cases}$, may serve as examples. The relations of these substances to ammonia and to acetic acid are shown by the formulas, ordinary or mon-acetamide being $NH_2.C_2H_3O$ or $CH_3.CO.NH_2$.

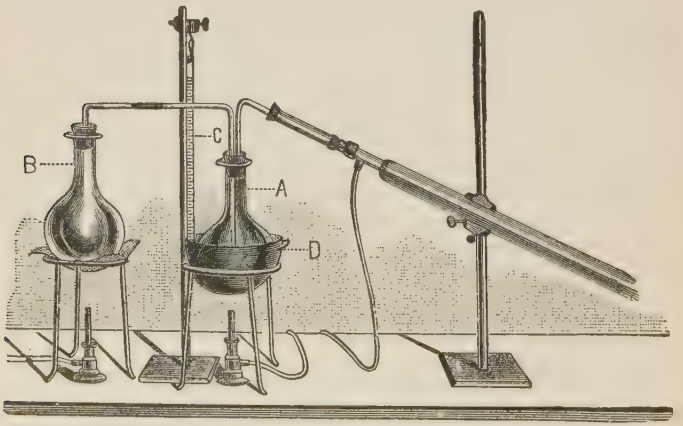


Fig. 12.

Experiment 45. Arrange an apparatus as shown in Fig. 12. In flask *A* put 50^g oxalic acid (dehydrated at 100°) and 50^g absolute alcohol; and, in flask *B*, 50^g absolute alcohol. Heat the bath *D* to 100°; and then heat the alcohol in flask *B* to boiling, and continue to pass

the vapor from flask *B* into the mixture in flask *A*, meanwhile allowing the temperature of the oil-bath to rise to 125°–130°. A mixture of alcohol and ethyl oxalate will distil over, while the ethyl oxalate will be mostly in flask *A*. Add concentrated ammonia to some of the ethyl oxalate. Oxamide is thrown down as a white powder. What reactions have taken place? Write the equations. Filter off the oxamide, and wash it with water. See whether it conducts itself like an acid. Has it an acid reaction? Boil with caustic potash (not too much), and notice whether ammonia is given off. Why does it dissolve? How can the oxalic acid be extracted from the solution?

When the amide of a poly-basic acid is boiled with ammonia, and under some other circumstances, partial decomposition takes place, and a substance is formed which is both amide and acid. Thus, in the case of oxamide, the product is *oxamic acid*, $\begin{matrix}CO_2H\\|\\CONH_2\end{matrix}$. This acid forms well-characterized salts and other derivatives such as are obtained from acids in general. There is one acid of this kind which is a well-known natural substance. It has already been referred to in connection with aspartic acid, which is closely related to it. It is

Asparagine, amino-succinamic acid,

$C_4H_8N_2O_3 + H_2O\left(\begin{matrix}CH_2\cdot CONH_2\\|\\CH(NH_2)\cdot COOH\end{matrix}\right)$. — Asparagine is found in many plants, as in asparagus, liquorice, beets, peas, beans, vetches, and in wheat. It can be made by treating mon-ethyl amino-succinate with ammonia.

Note for Student. — What reaction takes place? Write the equation.

Asparagine forms large rhombic crystals, difficultly soluble in cold water, more easily in hot water. When boiled with acids or alkalies, it is converted into aspartic acid and ammonia.

Note for Student. — Notice that only the amino group of the amide is driven out of the compound by this treatment. The other amino group which is contained in the hydrocarbon portion of the compound is not affected.

Nitrous acid converts asparagine into malic acid.

Asparagine contains an asymmetric carbon atom, and two of the three theoretically possible stereoisomeric varieties are known. The levo-rotatory variety is found in the seeds of many plants, in asparagus, in beets, in peas, beans, and in vetch sprouts. The dextro-variety is also found in vetch sprouts. The inactive variety is not formed when the two active varieties are brought together in solution.

Succinimide, $C_2H_4 < \begin{matrix} CO \\ CO \end{matrix} > NH$. — This compound deserves attention in this connection, as it represents a not uncommon class known as the *acid imides*. They are formed from polybasic acids, most simply from dibasic acids. They may be regarded as the anhydrides in which the imino group has been substituted for an oxygen atom. They are formed from the amides by loss of ammonia. Thus: —

$$\begin{matrix} CH_2.CONH_2 \\ | \\ CH_2.CONH_2 \\ \text{Succinamide.} \end{matrix} = \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix} \!\!> NH + NH_3. \qquad \text{Succinimide.}$$

The hydrogen atom of the imide is replaceable to some extent by metals, or the imide has the properties of a weak acid.

Cyan-amides, CN_2H_2. — In speaking of cyanic acid, the existence of two chlorides of cyanogen was mentioned: one a liquid, having the formula NCCl; the other a solid, of the formula $N_3C_3Cl_3$. When the former is treated with ammonia, it is converted into an amide, $NC.NH_2$, which bears to cyanic acid, NC.OH, the relation of an amide. Like the other simple compounds of cyanogen, cyan-amide readily undergoes change. When simply kept unmolested, it is converted into *di-cyan-diamide*, $C_2N_4H_4$; while, when heated to 150°, a violent reaction takes place, and *tri-cyan-triamide*, $C_3N_6H_6$, is formed. The latter compound is also called *melamine* and *cyanuramide*, and from certain methods of formation it is concluded that it is

the amide of cyanuric acid. It is a strong mon-acid base. The formation of these compounds is particularly interesting, as illustrating the tendency on the part of the simpler cyanides to undergo change under slight provocation.

Guanidine, CN_3H_5. — This substance, which is closely related to cyan-amide, is formed by the oxidation of guanine (which see), and this in turn is obtained from guano. It can also be made by treating cyanogen iodide with ammonia: —

$$NCI + 2\,NH_3 = (NH)C < \begin{matrix} NH_2 \\ NH_2 . HI \end{matrix},$$

the product being the hydriodic acid salt of guanidine. As will be seen, guanidine is cyan-amide plus ammonia: —

$$NC . NH_2 + NH_3 = (NH)C < \begin{matrix} NH_2. \\ NH_2 \end{matrix}$$

It is a strongly alkaline base. Boiled with dilute sulphuric acid or baryta water, it yields urea and ammonia: —

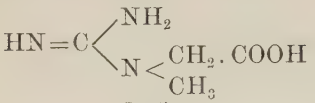
$$\underset{\text{Guanidine.}}{CN_3H_5} + H_2O = \underset{\text{Urea.}}{CON_2H_4} + NH_3.$$

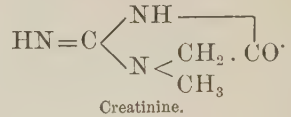
Creatine, $C_4H_9N_3O_2$. — This substance is found in the muscles of all animals. It is closely related to guanidine and also to sarcosine (see p. 205). It has been made synthetically by bringing cyan-amide and sarcosine together. The reaction which takes place is analogous to that made use of for the preparation of guanidine:

$$\underset{\text{Cyan-amide.}}{N \equiv C - NH_2} + \underset{\text{Sarcosine.}}{\begin{matrix} HN . CH_3 \\ | \\ H_2C . CO_2H \end{matrix}} = HN = C \begin{matrix} \diagup NH_2 \\ \diagdown N < \begin{matrix} CH_2 . COOH. \\ CH_3 \end{matrix} \end{matrix}$$
$$\text{Creatine.}$$

Creatinine, $C_4H_7N_3O$, is in small quantity a constant constituent of urine. It can be made from creatine by evaporating its solutions, especially if acids are present. In contact with alkalies it gradually takes up the elements of

water and forms creatine. It is a strong base, forming with acids well crystallized salts. Its relation to creatine is represented thus: —


Creatine.


Creatinine.

Urea, or carbamide and derivatives. — Closely related to the nitrogen compounds just considered is urea, or the amide of carbonic acid. Its importance and certain peculiarities distinguish it from the other acid amides, and it is therefore treated of by itself.

Urea is found in the urine and blood of all mammals, and particularly in the urine of carnivorous animals. Human urine contains from 2 to 3 per cent; the quantity given off by an adult man in 24 hours being about 30g. Urea can be made by the following methods: —

(1) By treating carbonyl chloride with ammonia: —

$$COCl_2 + 2\,NH_3 = CON_2H_4 + 2\,HCl.$$

What is the analogous reaction for the preparation of acetamide?

(2) By heating ammonium carbamate: —

$$CO{<}\begin{matrix}NH_2\\ONH_4\end{matrix} = CON_2H_4 + H_2O.$$

What is the analogous reaction for preparing oxamide?

(3) By treating ethyl carbonate with ammonia: —

$$CO{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + 2\,NH_3 = CON_2H_4 + 2\,C_2H_6O.$$

(4) By the addition of water to cyan-amide: —

$$CN\,.\,NH_2 + H_2O = CON_2H_4.$$

(5) By evaporation of ammonium cyanate in aqueous solution: —

$$CN(ONH_4) = CON_2H_4.$$

This reaction is of special interest, for the reason that it afforded the first example of the formation, by artificial methods from inorganic substances, of an organic compound found in the animal body (see p. 1).

Urea is most readily obtained from urine.

Experiment 46. Evaporate four or five litres *fresh* urine to a thin, syrupy consistence. After cooling add ordinary concentrated nitric acid, when crystals of urea nitrate are obtained. Filter, wash, and recrystallize from moderately concentrated nitric acid. When the crystals of urea nitrate are white, dissolve again in water, and add finely-powdered barium carbonate. The nitric acid forms barium nitrate, and the urea is left in free condition. Evaporate to dryness, and from the residue extract the urea with strong alcohol.

Experiment 47. Make potassium cyanate as directed in Experiments 24, p. 82, and 26, p. 84. Extract the cyanate with *cold* water, and add a solution of ammonium sulphate containing as much of the salt as there was used of potassium ferrocyanide in the preparation of the cyanate. Evaporate to a small volume, and allow to cool. Potassium sulphate will crystallize out. Filter this off, and evaporate to dryness. Extract with alcohol. The urea will crystallize from the alcoholic solution when it is brought to the proper concentration. Give all the reactions involved in passing from potassium ferrocyanide to urea. Compare the urea made artificially with that made from urine.

Urea crystallizes from alcohol in large rhombic prisms, which melt at 132°.

Experiment 48. Determine the melting-points of both the natural and artificial specimens of urea.

Urea is easily soluble in water and alcohol. Heated with water in a sealed tube to 100°, or boiled with dilute acid or alkalies, it breaks up into carbon dioxide and ammonia: —

$$CON_2H_4 + H_2O = CO_2 + 2\,NH_3.$$

The same decomposition of the urea takes place spontaneously when urine is allowed to stand. Hence the odor of ammonia is always noticed in the neighborhood of urinals which are not kept thoroughly clean. This decomposition is due to the action

of an organism known as *micrococcus ureæ.* This change is a good example of the way in which nature converts useless material into useful ones. Urea is a waste-product of the life-process. After it has left the body it ceases to be of value, whereas carbon dioxide and ammonia are of importance for the life of plants and animals.

Sodium hypochlorite or hypobromite decomposes urea into carbon dioxide, nitrogen, and water.

$$CO(N_2H_4) + 3\,NaOCl = CO_2 + 3\,NaCl + N_2 + 2\,H_2O.$$

The carbon dioxide can be absorbed by a solution of potassium hydroxide and the nitrogen then measured. From the volume of nitrogen obtained the amount of urea can be deduced. This is the basis of one of the methods used for estimating urea.

Experiment 49. To a solution of 20^g sodium hydroxide in 100^{cc} water add about 5^{cc} bromine, and shake well. Make a solution of urea in water, and add to the solution of the hypobromite. An evolution of gas will be noticed, showing that the urea is decomposed.

Nitrous acid acts in the same way: —

$$CON_2H_4 + 2\,HNO_2 = CO_2 + 2\,N_2 + 3\,H_2O.$$

When heated, urea loses ammonia, and yields first *biuret,* and finally *cyanuric acid* (see p. 85): —

$$\begin{array}{l} OC < \begin{array}{l} NH_2 \\ NH \\ NH_2 \end{array} \\ OC < \begin{array}{l} \boxed{H} \\ \boxed{NH_2} \\ NH_2 \end{array} \end{array} = \begin{array}{l} OC < \begin{array}{l} NH_2 \\ NH \\ NH_2 \end{array} + NH_3 \\ OC < \end{array}$$

Urea. Biuret.

$$3\,CO(NH_2)_2 = C_3H_3O_3N_3 + 3\,NH_3.$$

Cyanuric acid.

Urea unites with acids, bases, and salts. The hydrogen of the amino groups can be replaced by acid or alcohol radicals, giving compounds of which *acetyl urea,* $CO<\begin{array}{l} NH.C_2H_3O \\ NH_2 \end{array}$, and *ethyl urea,* $CO<\begin{array}{l} NHC_2H_5 \\ NH_2 \end{array}$, are examples.

Among the compounds with acids, the following may be mentioned: *urea hydrochloride*, $CH_4N_2O.HCl$; *urea nitrate*, $CH_4N_2O.HNO_3$; and *urea phosphate*, $CH_4N_2O.H_3PO_4$. With metals it forms such compounds as that with *mercuric oxide*, $HgO.CH_4N_2O$; with *silver*, $CH_2N_2O.Ag_2$, etc. With salts it forms such compounds as $HgCl_2.CH_4N_2O$, $HgO.CH_4N_2O.HNO_3$, etc.

Substituted ureas — that is, those derivatives of urea which contain hydrocarbon residues in place of one or all the hydrogen atoms — can be made from the cyanates of substituted ammonias. The fundamental reaction is the spontaneous transformation of ammonium cyanate into urea: —

$$CN.ONH_4 = CO(NH_2)_2.$$

In the same way, cyanates of substituted ammonias are transformed into substituted ureas: —

$$CN.ONH_3C_2H_5 = CO<\begin{matrix}NHC_2H_5\\NH_2\end{matrix};$$

$$CN.ONH_2(C_2H_5)_2 = CO<\begin{matrix}N(C_2H_5)_2\\NH_2\end{matrix}, \text{ etc.}$$

The urea derivatives which contain acid radicals are made by treating urea with the acid chlorides: —

$$CO<\begin{matrix}NH_2\\NH_2\end{matrix} + C_2H_3OCl = CO<\begin{matrix}NH.C_2H_3O\\NH_2\end{matrix} + HCl.$$

Acetyl urea.

Note for Student. — In what sense is acetyl urea analogous to acetamide?

Ureids are compounds derived from urea by the substitution of acid residues for one or more of the hydrogen atoms. Thus, acetyl urea, $OC<\begin{matrix}NH.OC.CH_3\\NH_2\end{matrix}$, is a simple ureid. The relation between the acid and urea in the ureid is like that between the acid and ammonia in the amide: —

$$\underset{\text{Acid.}}{CH_3.COOH} + HH_2N = \underset{\text{Amide.}}{CH_3.CONH_2} + H_2O;$$

$$\underset{\text{Acid.}}{CH_3.COOH} + \underset{H_2N}{\overset{\text{Urea.}}{HHN}}\!>\!CO = \underset{H_2N}{\overset{\text{Ureid.}}{CH_3.COHN}}\!>\!CO + H_2O.$$

The ureids of dibasic acids resemble in the same way the amides of these acids. One urea residue takes the place of the two acid hydroxyls. Thus, in the case of oxalic acid the relation is shown by the formulas below: —

$$\underset{\text{Oxalic acid.}}{\begin{matrix}COOH\\COOH\end{matrix}} + \underset{\text{Urea.}}{\begin{matrix}HHN\\HHN\end{matrix}}\!>\!CO = \underset{\text{Ureid of oxalic acid.}}{\begin{matrix}CO.HN\\|\\CO.HN\end{matrix}}\!>\!CO + 2\,H_2O.$$

There are several compounds of this kind that are of importance: —

Parabanic acid,
Oxalyl urea,
Oxal-ureid,
$\Big\}\ C_3H_2N_2O_3\ \Big\{ = \begin{matrix}CO.HN\\|\\CO.HN\end{matrix}\!>\!CO \Big\}$. — This is formed by boiling uric acid with strong nitric acid and with other oxidizing agents, and by treating a mixture of oxalic acid and urea with phosphorus oxychloride. It acts like an acid, the hydrogen of the imide group being replaceable by metals as in succinimide. Its salts readily pass over into salts of oxaluric acid when treated with water: —

$$\begin{matrix}CO.HN\\|\\CO.HN\end{matrix}\!>\!CO + H_2O = \begin{matrix}COOH\\|\\CO.HN.CONH_2.\end{matrix}$$

Oxaluric acid, $C_3H_4N_2O_4\left(= \begin{matrix}CO.OH\\|\\CO.HN.CO.NH_2\end{matrix}\right)$, bears to parabanic acid the same relation that oxamic acid bears to oxamide. It occurs in the form of the ammonium salt in small quantity in human urine. With phosphorus oxychloride it gives parabanic acid.

Barbituric acid, malonyl urea,
$C_4H_4N_2O_3 + 2\,H_2O \left(= CH_2 < \begin{matrix} CO \cdot NH \\ CO \cdot NH \end{matrix} > CO \right)$. — Barbituric acid, like parabanic acid, is a product obtained from uric acid. It has been made artificially by treating a mixture of malonic acid and urea with phosphorus oxychloride: —

$$CH_2 < \begin{matrix} COOH \\ COOH \end{matrix} + CO < \begin{matrix} NH_2 \\ NH_2 \end{matrix} = CH_2 < \begin{matrix} CO \cdot NH \\ CO \cdot NH \end{matrix} > CO + 2\,H_2O.$$

Treated with an alkali, barbituric acid breaks up into malonic acid and urea.

The relation of the acid to malonic acid and urea is the same as that of parabanic acid to oxalic acid and urea.

Sulpho-urea, Thio-urea, $CS(NH_2)_2$. — This substance is formed by heating ammonium sulpho-cyanate, the reaction which takes place being analogous to that by which urea is formed from ammonium cyanate: —

$$NCSNH_4 = SC(NH_2)_2.$$

It forms rhombic prisms melting at 172°. It combines with one equivalent of acids, forming salts.

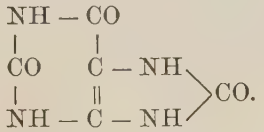
A number of derivatives of sulpho-urea have been made. They resemble those obtained from urea.

Uric acid, $C_5H_4N_4O_3$. — Uric acid occurs in human urine in small quantity, in the urine of carnivorous animals, and in the excrement of birds and of reptiles. The excrement of reptiles consists almost wholly of ammonium urate. In gout, uric acid is deposited in the joints, under the skin, and in the bladder as calculi, in the form of insoluble acid salts.

Uric acid forms colorless, crystalline scales, and is almost insoluble in water. It acts like a weak dibasic acid.

By treating the lead salt of uric acid with methyl iodide, two isomeric methyl-uric acids can be obtained, and these can be further converted into a tetra-methyl-uric acid, which is derived from uric acid by the substitution of four methyl

groups for the four hydrogen atoms, $C_5(CH_3)_4N_4O_3$. When this is decomposed, all the methyl groups are given off in combination with nitrogen as methyl-amine. This shows that uric acid contains four imine groups, as shown in the formula $C_5(NH)_4O_3$. Other transformations show that the constitution of the acid must be represented by the formula



According to this, uric acid contains two urea residues combined in different ways with the group . It is to be regarded as a diureid of a trihydroxyacrylic acid, $C(OH)_2 = C(OH) . CO_2H$. That this view is correct has been shown by the artificial preparation of the acid.

It will be seen that uric acid contains residues not only of urea, but of parabanic acid, of barbituric acid, and of a ureid of mesoxalic acid (alloxan).

Xanthine, $C_5H_4N_4O_2$, is found in all the tissues of the body and in the urine, in some rare urinary calculi, and in several animal liquids. It is formed by the action of nitrous acid on guanine: —

$$C_5H_5N_5O + HNO_2 = C_5H_4N_4O_2 + H_2O + N_2.$$

In this case the nitrous acid causes a substitution of an oxygen atom for an imine group.

Theobromine, Dimethyl-xanthine, $C_7H_8N_4O_2[= C_5H_2(CH_3)_2N_4O_2]$, is a substance found in chocolate prepared from the seed of the cacao tree. It has been made by treating the lead compound of xanthine with methyl iodide.

Caffeine, theine, trimethyl-xanthine,

$C_8H_{10}N_4O_2 + H_2O[= C_5H(CH_3)_3N_4O_2 + H_2O]$, is the active constituent of coffee and tea. It has been made from theobromine by the introduction of a third methyl group.

Thus, as will be seen, a close connection is established between the active constituents of coffee, tea, and chocolate on the one hand, and xanthine and guanine on the other.

Guanine, $C_5H_5N_5O[= C_5H_3(NH_2)N_4O]$, is found principally in guano, from which it is prepared. Nitrous acid converts it into xanthine. Oxidizing agents convert it into guanidine, CN_3H_5 (see p. 213).

Retrospect.

Before passing on to the next division of our subject, it will be well to recall briefly what we have thus far learned.

In the first place, all the compounds which we have considered may be regarded as derived from the marsh-gas hydrocarbons or paraffins.

By replacing the hydrogen atoms of these hydrocarbons with chlorine, bromine, or iodine, we get (1) *the substitution-products of the hydrocarbons.*

By introducing hydroxyl into a hydrocarbon in place of hydrogen, we get the bodies called (2) *alcohols*, of which there are three classes: (*a*) the *primary*, (*b*) the *secondary*, and (*c*) the *tertiary alcohols.*

By oxidizing primary alcohols we get (3) *aldehydes.*

By oxidizing secondary alcohols we get (4) *ketones.*

By oxidizing alcohols, aldehydes, and ketones, we get (5) *acids.*

Acids and alcohols act upon each other, forming (6) *ethereal salts*, and alcohols can be converted into (7) *ethers.*

Corresponding to the oxygen derivatives, we met with compounds containing sulphur, as (8) the *sulphur alcohols*, or *mercaptans;* (9) the *sulphur ethers;* and (10) the *sulphonic acids.*

Next, we found compounds containing nitrogen. Under this head we considered *cyanogen*, and the allied compounds *hydrocyanic*, *cyanic*, and *sulpho-cyanic acids*. Allied to these we found (11) the *cyanides*, and (12) the *isocyanides;* (13) the *cyanates*, and (14) the *isocyanates;* (15) the *sulpho-cyanates*, and (16) the *iso-sulpho-cyanates* or *mustard oils*.

Finally, we found (17) *compounds containing metals in combination with radicals*.

Representatives of these various classes of compounds were studied, and the relations between them pointed out.

We found *poly-acid alcohols* and *poly-basic acids*.

Under the head of *mixed compounds* were found compounds which belong at the same time to two or more of the fundamental classes, as the *hydroxy-acids*, the *carbo-hydrates*, and the *amino-acids*. A consideration of the amino-acids and the acid amides brought us naturally to the consideration of urea and its derivatives, and of uric acid and its derivatives.

We turn now to a new class of compounds, known as *unsaturated compounds*.

CHAPTER XIII.

UNSATURATED CARBON COMPOUNDS. — DISTINCTION BETWEEN SATURATED AND UNSATURATED COMPOUNDS.

Most of the compounds thus far studied are generally called *saturated compounds*. This is certainly an appropriate name so far as the hydrocarbons themselves and some of the classes of their derivatives are concerned. The expression "saturated" is intended to signify that the compounds have no power to unite directly with other compounds or elements. Thus marsh gas cannot be made to unite directly with anything. Bromine, for example, must first displace hydrogen before it can enter into combination: —

$$CH_4 + Br_2 = CH_3Br + HBr.$$

The compound is saturated.

On the other hand, a compound which can take up elements or other compounds directly is called *unsaturated*. Thus, phosphorus trichloride is unsaturated, for it has the power to take up two chlorine atoms, thus: —

$$PCl_3 + Cl_2 = PCl_5.$$

Ammonia is unsaturated, for it can take up an equivalent of an acid: —

$$NH_3 + HCl = NH_4Cl.$$

The condition of unsaturation is met with among carbon compounds in several forms: —

First. The aldehydes act like unsaturated compounds, as shown in their power to take up ammonia, hydrocyanic acid, and other substances.

Second. The ketones also act like unsaturated compounds, though their power in this way is less marked than that of the aldehydes.

Third. The substituted ammonias are unsaturated, in the same sense in which ammonia itself is unsaturated.

Fourth. The cyanides take up hydrogen directly, and are therefore unsaturated also.

In the substituted ammonias the unsaturation is due to the same cause as that in ammonia. In them the nitrogen is trivalent. In contact with acids it becomes quinquivalent, and saturates itself.

In the cyanides carbon and nitrogen are probably linked together in a different way from that in the substituted ammonias, and when hydrogen is added to the cyanogen group, $-C\equiv N$, the condition is changed to that which is characteristic of the substituted ammonias: —

$$H-C\equiv N + 2\,H_2 = H_3C-NH_2.$$

In the aldehydes and ketones, carbon is in combination with oxygen in the carbonyl condition. When they unite with hydrogen and some compounds, such as hydrocyanic acid, the relation between the carbon and oxygen is probably changed to the hydroxyl condition. The changes are usually represented by formulas such as the following: —

$$CH_3.C\begin{cases}O\\H\end{cases} + H_2 = CH_3.C\begin{cases}OH\\H_2\end{cases},$$

$$(CH_3)_2C=O + HCN = (CH_3)_2C\begin{cases}CN\\OH\end{cases}.$$

In carbonyl the oxygen is represented as held by two bonds to the carbon atom, while in hydroxyl it is represented as held by one bond. The signs may be used if not too literally interpreted. There are undoubtedly two relations which carbon and oxygen bear to each other in carbon compounds. These relations may be called *the hydroxyl relation*, represented by the sign C — O — , and *the carbonyl relation*, represented by the sign C = O.

Fifth. There is a fifth kind of unsaturation, *dependent upon differences in the relations between carbon atoms*, and it is this kind which is ordinarily meant when *unsaturated carbon compounds* are spoken of.

The kind of relation between the carbon atoms in all the saturated hydrocarbons is, so far as we know, the same as that which exists between the two carbon atoms of ethane, and this is represented by the formula $H_3C - CH_3$. This formula signifies simply that the two carbon atoms are held together by the forces which in marsh gas enabled each methyl group to hold one hydrogen atom. Abstracting *one hydrogen atom* from marsh gas, union is effected between the carbon atoms. What would result if *two hydrogen atoms* were to be abstracted, and union between the carbons then effected? Theoretically we should get a compound made up of two groups CH_2, thus $CH_2.CH_2$, and presumably the relation between the carbon atoms in this compound would be different from the relation between the carbon atoms in ethane. Without pushing these speculations farther, it may be said that there is a well-known hydrocarbon of the formula C_2H_4 which differs markedly from ethane. It shows the property of unsaturation very clearly. This is *olefiant gas* or *ethylene*. It is the first of an homologous series of hydrocarbons, only a few of which are well known. These hydrocarbons yield derivatives like the paraffins; though of these, as well as of the hydrocarbons, very few are known as compared with the number of the paraffin derivatives.

ETHYLENE AND ITS DERIVATIVES.

Hydrocarbons, C_nH_{2n}, the Olefines.

The principal hydrocarbons of this series are included in the subjoined table: —

Ethylene,	Ethene	C_2H_4.
Propylene,	Propene	C_3H_6.
Butylene,	Butene	C_4H_8.
Amylene,	Pentene	C_5H_{10}.
Hexylene,	Hexene	C_6H_{12}.
Heptylene,	Heptene	C_7H_{14}.

The members are homologous with ethylene. They bear to the paraffins a very simple relation, each one containing two atoms of hydrogen less than the paraffin with the same number of carbon atoms.

Ethylene, olefiant gas, $C_2H_4(=CH_2.CH_2)$. — This gas is formed when many organic substances are subjected to dry distillation. The two principal reactions which yield it are: —

(1) The action of an alcoholic solution of potassium hydroxide on ethyl chloride, bromide, or iodide: —

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.$$

This is the most important reaction for the preparation of the unsaturated compounds of the ethylene series. It is applicable not only to the hydrocarbons but to substances belonging to other classes. By means of it we have it in our power to pass from any saturated compound to the corresponding unsaturated compound of the ethylene series. Thus we pass from ethane, C_2H_6, to ethylene, C_2H_4, by first introducing bromine, and then abstracting hydrobromic acid from the mono-bromine substitution-product. By treating the mono-bromine substitution-

products of other saturated compounds in the same way, the corresponding unsaturated compounds can be made.

(2) The action of sulphuric acid and other dehydrating agents upon alcohol: —

$$C_2H_5.OH = C_2H_4 + H_2O.$$

Experiment 51. In a flask of 2^l to 3^l capacity put a mixture of 25^g alcohol and 150^g ordinary concentrated sulphuric acid. Heat to 160° to 170°, and add gradually through a funnel tube about 500^{cc} of a mixture of 1 part of alcohol and 2 parts of concentrated sulphuric acid. Pass the gas through three wash bottles containing, in order, sulphuric acid, caustic soda, and sulphuric acid. Then pass it into bromine contained in a cylinder, provided with a cork with two holes. If the cylinder has a diameter of about 5^{cm}, let the layer of bromine be about 5^{cm} to 7^{cm} deep. Upon it pour a somewhat deeper layer of water. Place the cylinder in a vessel containing cold water. Pass the gas into the bromine until it is completely decolorized. (See note, next page.)

Ethylene is a colorless gas which can be condensed to a liquid. It burns with a luminous flame. With oxygen it forms a mixture which explodes when ignited. *Its most characteristic property is its power to unite directly with other substances, particularly with the halogens and with the hydrogen acids of the halogens.* Thus it unites with chlorine and bromine, and with hydriodic and hydrobromic acids: —

$$C_2H_4 + Cl_2 = C\,H_4Cl_2;$$
$$C_2H_4 + Br_2 = C_2H_4Br_2;$$
$$C_2H_4 + HBr = C_2H_5Br;$$
$$C_2H_4 + HI = C_2H_5I.$$

The products formed with chlorine and bromine are called *ethylene chloride* and *ethylene bromide.* They have been mentioned under the head of halogen derivatives of the paraffins. They are isomeric with *ethylidene chloride* and *ethylidene bromide*, which are formed by substitution of chlorine or bromine for two hydrogens of ethane.

NOTE. — The addition of bromine to ethylene is illustrated by the experiment last performed, in which ethylene bromide is formed. To purify the product, put a little dilute caustic soda in the cylinder, and shake. Remove the upper layer of water, and repeat the washing with dilute caustic soda. Then wash with water two or three times, each time removing the water with the aid of the pipette described on p. 31. Finally, put the oil in a flask, add a few pieces of granulated calcium chloride, and allow to stand. Pour off into a dry distilling-bulb, and distil, noting the temperature.

A question which we may fairly ask concerning the structure of ethylene is this: Does it consist of two groups CH_2, or of a methyl group, CH_3, and CH? Is it to be represented by the formula $CH_2.CH_2$ or $CH_3.CH$? Perhaps the clearest answer to this question is found in the fact that the chloride formed by addition of chlorine to ethylene, and that formed by replacing the oxygen in aldehyde by chlorine, are not identical. All evidence is in favor of the view that aldehyde is correctly represented by the formula $CH_3.C\overset{O}{\underset{H}{}}$. Hence, as has been pointed out, the chloride obtained from it must be represented thus, $CH_3.CHCl_2$. Hence, further, it appears highly probable that the isomeric chloride obtained from ethylene must be represented thus, $CH_2Cl.CH_2Cl$. Now, as this substance is formed by direct addition of chlorine to ethylene, ethylene has the formula $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$, and not $\begin{matrix} CH_3 \\ | \\ CH \end{matrix}$.

Nothing is known in regard to the relation between the two carbon atoms of ethylene, except that it is probably different from that which exists between the carbon atoms of ethane. It is usually represented by the sign $=$; thus, $\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$. We must necessarily leave the question open as to the relation between the carbon atoms in ethylene. If the above sign is used, it should serve mainly as an indication of the kind of unsaturation met with in ethylene, the compound in whose formula it is written having the power to take up two atoms of bromine, a molecule of hydrobromic acid, etc.

The homologues of ethylene bear the same relation to it that the homologues of ethane bear to this hydrocarbon. Propylene is methyl-ethylene, $\begin{matrix}CH.CH_3\\ \|\\ CH_2\end{matrix}$, just as propane is methyl-ethane, $\begin{matrix}CH_2.CH_3\\ |\\ CH_3\end{matrix}$. Butylene is dimethyl-ethylene, $\begin{matrix}CH.CH_3\\ \|\\ CH.CH_3\end{matrix}$, or $\begin{matrix}C(CH_3)_2\\ \|\\ CH_2\end{matrix}$, or ethyl-ethylene, $\begin{matrix}CH.C_2H_5\\ \|\\ CH_2\end{matrix}$. That is to say, in the hydrocarbons of the ethylene series the ethylene condition between carbon atoms occurs only once.

Alcohols, $C_nH_{2n}O$.

These alcohols bear to the ethylene hydrocarbons the same relation that the alcohols of the methyl alcohol series bear to the paraffins. Only one is well known. This is the second member, corresponding to propylene.

Allyl alcohol, C_3H_6O ($= CH_2{=}CH.CH_2OH$). — This alcohol is formed in several ways from glycerol.

1. By introducing two chlorine atoms into glycerol in the place of two hydroxyls, thus getting dichlorhydrin, $C_3H_5Cl_2.OH$:

$$\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix} + \begin{matrix}HCl\\ HCl\end{matrix} = \begin{matrix}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2OH\end{matrix} + 2\,H_2O;$$

and treating the dichlorhydrin with sodium, which extracts the chlorine: —

$$\begin{matrix}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2OH\end{matrix} + 2\,Na = \begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{matrix} + 2\,NaCl.$$

2. By treating glycerol with the iodide of phosphorus. This gives allyl iodide, C_3H_5I. By treating the iodide with silver hydroxide it is converted into the alcohol.

3. Most readily by treating glycerol with oxalic acid, as in the preparation of formic acid. The mixture is heated to 220° to 230°, when allyl alcohol passes over. The first product formed in this case is an ethereal salt of formic acid and glycerol, $HOH_2C.CHOH.CH_2O.COH$. At a higher temperature this breaks down, yielding allyl alcohol, $HOH_2C.CH = CH_2$, carbon dioxide and water.

Allyl alcohol is a colorless liquid boiling at 96.5°. It has a disagreeable penetrating odor and is miscible with water in all proportions.

Nascent hydrogen does not act upon it, or at least the action, if any, takes place with difficulty. As far as composition is concerned, the relation between allyl alcohol and propyl alcohol is the same as that between ethylene and ethane: —

$$C_3H_5.OH + H_2 = C_3H_7.OH.$$

Allyl alcohol forms esters with acids and gives the other reactions for alcoholic hydroxyl. It is, further, a primary alcohol, as it is converted by certain oxidizing agents into the corresponding aldehyde (acroleïn) and acid (acrylic acid).

When treated with a dilute solution of potassium permanganate it is converted into glycerol: —

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} \quad + O + H_2O = \begin{array}{l} CH_2OH \\ | \\ CHOH. \\ | \\ CH_2OH \end{array}$$

Allyl compounds. — Among the derivatives of allyl alcohol which are of special interest is *allyl sulphide*, $(C_3H_5)_2S$, which is the chief constituent of the *oil of garlic*. It can be made artificially by treating allyl iodide with potassium sulphide: —

$$2\,C_3H_5I + K_2S = (C_3H_5)_2S + 2\,KI.$$

It is a colorless, oily liquid of a disagreeable odor, only slightly soluble in water.

Allyl mustard oil, SCN.C_3H_5.—Under the head of Sulpho-cyanates mention was made of a series of isomeric compounds called *isosulpho-cyanates* or *mustard oils*. The sulpho-cyanates of the alcohol radicals are made from potassium sulpho-cyanate. Thus, methyl sulpho-cyanate is made by mixing together potassium methyl-sulphate and potassium sulpho-cyanate, and distilling:—

$$NCSK + \left.\begin{matrix} CH_3O \\ KO \end{matrix}\right\} SO_2 = K_2SO_4 + NCSCH_3.$$

The mustard oils, on the other hand, are made by a complicated reaction from carbon disulphide and substituted ammonias. The conduct of the sulpho-cyanates led to the conclusion that they must be represented by the formula NC – SR, while that of the isosulpho-cyanates or mustard oils led to the formula SC – NR, as representing their structure. Allyl mustard oil is the chief representative of the class of bodies known as mustard oils. It occurs as a glucoside (see p. 185) in mustard seed. From the glucoside it is formed by fermentation. It also occurs in horse-radish. It is formed by treating allyl iodide with potassium sulpho-cyanate. If this reaction consisted simply in the substitution of the allyl group, C_3H_5, for potassium the product should be allyl sulpho-cyanate, $C_3H_5S - CN$. As a matter of fact it is the isosulpho-cyanate $C_3H_5N - CS$. As has already been pointed out (see p. 91), the sulpho-cyanates are converted into the isosulpho-cyanates by heat, so that the formation of the isosulpho-cyanate in this case is not surprising.

Allyl mustard oil is a liquid, boiling at 150.7°, and having a very pungent odor.

Zinc and hydrochloric acid convert it into allyl-amine, $NH_2.C_3H_5$, and thioformic aldehyde, H_2CS. This reaction

indicates that in allyl mustard oil the radical allyl is in combination with the nitrogen and not with the sulphur.

NOTE FOR STUDENT. — What change do the mustard oils in general undergo when treated with nascent hydrogen? What change do the sulpho-cyanates undergo when oxidized?

Acroleïn, acrylic aldehyde, C_3H_4O ($= C_2H_3.COH$). — Acroleïn can be made by careful oxidation of allyl alcohol. It is formed by the dry distillation of impure glycerol, which breaks up into water and acroleïn: —

$$C_3H_8O_3 = C_3H_4O + 2\ H_2O.$$

It is, hence, formed also by heating the ordinary fats, the peculiar penetrating odor noticed when fatty substances are heated to a sufficiently high temperature being due to the formation of acroleïn. It is prepared best by heating glycerol with acid potassium sulphate.

Experiment 52. In a test-tube mix anhydrous glycerol (1 part) and acid potassium sulphate (2 parts), and heat the mixture. Pass the vapors through a bent tube into water contained in another test-tube. Notice the odor. Try the effect on a dilute solution of nitrate of silver. What is the meaning of this reaction?

Acroleïn is a volatile liquid which boils at 52.4°. It has an extremely penetrating odor, and its vapor acts violently upon the eyes, causing the secretion of tears.

Acroleïn takes up oxygen from the air, and is converted into the corresponding acid, *acrylic acid*, $C_3H_4O_2$ (which see).

It takes up hydrogen, and is thus converted into allyl alcohol.

It takes up hydrochloric acid, and is converted into β-chlor-propionic aldehyde: —

$$C_2H_3.COH + HCl = CH_2Cl.CH_2.COH.$$

β-Chlor-propionic aldehyde.

The first two reactions are characteristic of aldehydes in general; the last one is characteristic of unsaturated compounds belonging to the ethylene group. Acroleïn, like ordinary alde-

hyde, forms polymeric modifications which can easily be reconverted into acroleïn.

It unites with ammonia, forming acroleïn-ammonia, and with other substances in much the same way as ordinary aldehyde does. It unites with bromine to form acroleïn dibromide, which when treated with barium hydroxide gives *i*-fructose (which see).

Acids, $C_nH_{2n-2}O_2$.

Running parallel to the ethylene series of hydrocarbons, and bearing the same relation to it that the fatty acid series bears to the paraffins, is a series of acids of which the first member is acrylic acid, $C_3H_4O_2$. Several members of the series are known. The principal members are named in the subjoined table: —

ACRYLIC ACID SERIES.

Acids, $C_nH_{2n-2}O_2$.	
Acrylic acid	$C_3H_4O_2$.
Crotonic "	$C_4H_6O_2$.
Angelic "	$C_5H_8O_2$.
Hydrosorbic "	$C_6H_{10}O_2$.
Teracrylic "	$C_7H_{12}O_2$.
Cimic "	$C_{15}H_{28}O_2$.
Hypogæic "	$C_{16}H_{30}O_2$.
Oleïc "	$C_{18}H_{34}O_2$.
Erucic "	$C_{22}H_{42}O_2$.

Of most of the higher members of the series several isomeric modifications are known. Only a few of these acids will be considered here.

Acrylic acid, $C_3H_4O_2(CH_2{=}CH\cdot CO_2H)$. — This acid has already been mentioned in connection with hydracrylic acid, which, when heated, breaks up into acrylic acid and water: —

$$\underset{\text{Hydracrylic acid.}}{CH_2.OH.CH_2.CO_2H} = \underset{\text{Acrylic acid.}}{CH_2.CH.CO_2H} + H_2O.$$

NOTE FOR STUDENT. — This reaction is analogous to that which takes place when ordinary alcohol is converted into ethylene. In what does the analogy consist? What acid is isomeric with hydracrylic acid? How does it conduct itself when heated? Compare the transformation of hydracrylic acid into acrylic acid with that of malic into maleïc and fumaric acids, and with that of citric into aconitic acid.

Acrylic acid can be made by careful oxidation of acroleïn with silver oxide. The relations between propylene, C_3H_6, allyl alcohol, $C_3H_5.OH$, acroleïn, $C_2H_3.COH$, and acrylic acid, $C_2H_3.CO_2H$, are the same as those between any hydrocarbon of the paraffin series, and the corresponding *primary* alcohol, aldehyde, and acid.

Acrylic acid can be made further by treating β-iodo-propionic acid with alcoholic caustic potash:—

$$CH_2I.CH_2.CO_2H = CH_2.CH.CO_2H + HI.$$

NOTE FOR STUDENT. — Compare this reaction with that by which ethylene is made from ethyl bromide.

Acrylic acid is a liquid having a pungent odor. It boils at 140°, and solidifies at 7°.

Nascent hydrogen converts it into propionic acid. Hydriodic acid unites directly with it, forming β-iodo-propionic acid.

NOTE FOR STUDENT. — What are the analogous reactions with allyl alcohol and acroleïn?

Crotonic acid, $C_4H_6O_2$. — Ordinary or solid crotonic acid is formed, (1) By hydrolyzing allyl cyanide; (2) By distilling β-hydroxy-butyric acid; (3) By treating α-brom-butyric acid with alcoholic caustic potash; (4) By heating malonic acid with paraldehyde and acetic anhydride.

Allyl cyanide must have the structure represented by the formula $CH_2=CH.CH_2.CN$, and we should naturally expect that the acid formed from it by hydrolysis would have the

formula $CH_2{=}CH.CH_2.CO_2H$. But, on the other hand, the abstraction of hydrobromic acid from α-brom-butyric acid, $CH_3.CH_2.CHBr.CO_2H$, should give an acid of the formula $CH_3.CH=CH.CO_2H$. So also the formation of crotonic acid from paraldehyde and malonic acid points to the formula $CH_3.CH=CH.CO_2H$ for crotonic acid:—

$$(1)\ \underset{\text{Aldehyde.}}{CH_3.CHO} + \underset{\text{Malonic acid.}}{CH_2{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}} = CH_3.CH=C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix} + H_2O;$$

$$(2)\ CH_3.CH=C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix} = \underset{\text{Crotonic acid.}}{CH_3.CH=CH.CO_2H} + CO_2.$$

Again, when crotonic acid is fused with caustic potash, it gives only acetic acid:—

$$C_4H_6O_2 + H_2O + O = 2\,C_2H_4O_2;$$

and, as it has been shown that under these circumstances the breaking down takes place at the place where the double bond occurs, this reaction furnishes additional evidence in favor of the view that ordinary crotonic acid has the constitution represented by the formula $CH_3.CH=CH.CO_2H$.

From the above it seems probable that, when allyl cyanide is hydrolyzed, the position of the double bond is changed:

$$CH_2=CH.CH_2.CN \longrightarrow CH_3.CH=CH.CO_2H.$$

Isocrotonic acid appears to contain the same groups as crotonic acid, and is also to be represented by the formula:—

$$CH_3.CH=CH.CO_2H.$$

As will be shown under Maleïc and Fumaric Acids (which see), the difference between the two forms of crotonic acid is probably due to the arrangement of the constituents in space.

Oleïc acid, $C_{18}H_{34}O_2$.— This acid was referred to in connection with the fats, it being one of the three acids found most frequently in combination with glycerol. Oleïn, or

glyceryl tri-oleate, is the liquid fat, and is the chief constituent of the fatty oils, such as olive oil, whale oil, etc., and of the fats of cold-blooded animals. It is contained also in almost all ordinary fats. In the preparation of stearic acid for the manufacture of candles, the oleïc acid is pressed out of the mixture of fatty acids. To prepare the acid, oleïn is saponified, and the soap then decomposed with hydrochloric acid.

NOTE FOR STUDENT. — Give the equations representing the reactions involved in passing from oleïn, or glyceryl tri-oleate, to oleïc acid.

Oleïc acid is a crystallized substance that melts at 14°. It unites with bromine, forming dibromstearic acid. Hydriodic acid converts it into stearic acid: —

$$\underset{\text{Oleïc acid.}}{C_{18}H_{34}O_2} + H_2 = \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}.$$

POLYBASIC ACIDS OF THE ETHYLENE GROUP.

There are a few dibasic acids that bear to the ethylene hydrocarbons the same relations that the members of the oxalic acid series bear to the paraffins. They may be regarded as derived from the hydrocarbons by the introduction of two carboxyl groups.

Acids, $C_2H_2(CO_2H)_2$. — There are two acids of this formula, *fumaric* and *maleïc acids*, both of which are formed by the distillation of malic acid.

Fumaric acid can also be made by treating brom-succinic acid with alcoholic potash.

Both fumaric and maleïc acids are converted into succinic acid by nascent hydrogen, and into brom-succinic acid by hydrobromic acid: —

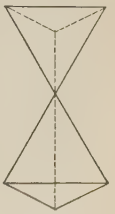
$$\underset{\text{Malic acid.}}{C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}} = \underset{\text{Maleïc or Fumaric acid.}}{C_2H_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}} + H_2O;$$

$$\underset{\text{Brom-succinic acid.}}{C_2H_3Br<\begin{matrix}CO_2H\\CO_2H\end{matrix}} = \underset{\text{Fumaric acid.}}{C_2H_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}} + HBr;$$

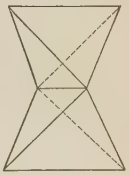
$$C_2H_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} + 2\,H = C_2H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$$

Maleïc or Fumaric acid. Succinic acid.

An extension of the fundamental ideas of stereochemistry furnishes an explanation of the relation between maleïc and fumaric acids. According to these ideas, a carbon atom in combination with four atoms or groups of atoms holds these atoms or groups by bonds directed toward the solid angles of a tetrahedron, the carbon atom itself being at the centre of the tetrahedron. When two carbon atoms unite in the simplest way, the stereochemical model representing the compound consists of two tetrahedrons united at one of the solid angles of each, thus: —

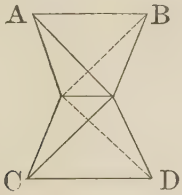


When two carbon atoms unite by a double bond, as in the ethylene compounds, the model consists of two tetrahedrons united by one of the edges of each, thus: —

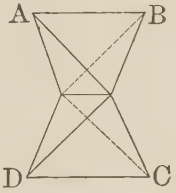


In case each carbon is in combination with two unlike atoms or groups, there are two ways in which these can be arranged in space, as shown by the figures: —

I.

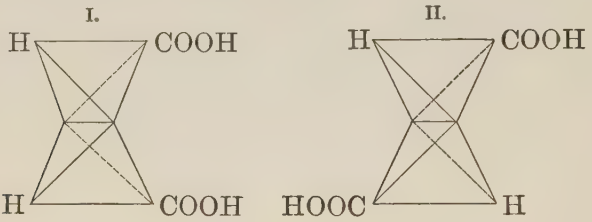


II.



It will be seen that, in the first of these figures, A and C are on one side, and B and D on the other side; while in the sec-

ond figure A and D are on one side and B and C on the other. The two arrangements are different. In maleïc and fumaric acids each carbon atom is in combination with one hydrogen atom and one carboxyl group, as shown by the ordinary formula $\begin{matrix}CH\,.\,CO_2H\\ \|\\ CH\,.\,CO_2H\end{matrix}$. These can be arranged in two ways corresponding to the above figures, thus: —



It is believed that figure I. represents the configuration of maleïc acid, and figure II. that of fumaric acid. The main reason for this is the fact that when maleïc acid is heated it loses water and forms an anhydride, while fumaric acid does not form an anhydride. As the anhydride is formed by the interaction of the two carboxyl groups, a substance of configuration I. could form an anhydride more easily than one of configuration II.

The configurations of maleïc and fumaric acids can be represented by formulas, thus: —

$$\begin{matrix}H-C-CO_2H\\ \|\\ H-C-CO_2H\end{matrix}$$

Maleïc acid.

$$\begin{matrix}H-C-CO_2H\\ \|\\ CO_2H-C-H\end{matrix}$$

Fumaric acid.

Maleïc anhydride similarly can be represented thus: —

$$\begin{matrix}H-C-CO\\ \|\quad\quad\rangle O\\ H-C-CO\end{matrix}$$

This extension of the theory of stereochemistry applies to a large number of phenomena and furnishes a satisfactory explanation of a number of cases of isomerism for which no other explanation has been found.

The two crotonic acids already referred to are believed to be related to each other in the same way as maleïc and fumaric acids, as shown by the formulas: —

$$\begin{array}{l} CH_3 - C - H \\ \quad\quad\| \\ CO_2H - C - H \end{array} \qquad \begin{array}{l} CH_3 - C - H \\ \quad\quad\| \\ H - C - CO_2H \end{array}$$

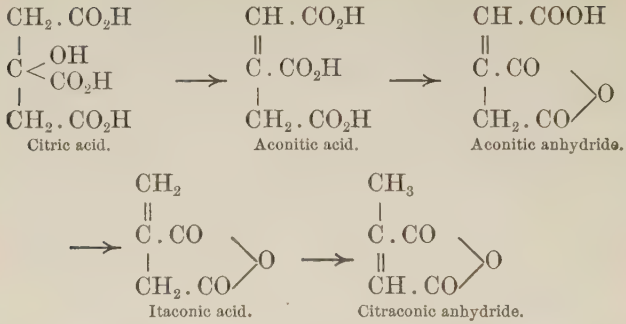
Acids, $C_5H_6O_4$. — When citric acid is rapidly heated, a distillate consisting of the anhydrides of two acids of the formula $C_5H_6O_4$ is obtained. These acids are *itaconic* and *citraconic acids*. When itaconic anhydride is distilled under ordinary pressure, it is converted into citraconic anhydride. When citraconic anhydride is heated for some time with water at 150°, itaconic acid is formed. When a water solution of citraconic anhydride is treated with hydrochloric or nitric acid and then evaporated, a third acid, *mesaconic acid*, isomeric with citraconic and itaconic acid, is obtained.

It has been shown that citraconic and mesaconic acids are respectively homologues of maleïc and fumaric acids, as represented by the formulas: —

$$\begin{array}{l} CH_3 - C - CO_2H \\ \quad\quad\| \\ H - C - CO_2H \end{array} \qquad \begin{array}{l} CH_3 - C - CO_2H \\ \quad\quad\| \\ CO_2H - C - H \end{array}$$

Citraconic acid. Mesaconic acid.

Like fumaric acid, mesaconic acid does not form an anhydride. Itaconic acid is not a methyl derivative of maleïc or fumaric acid, but corresponds to the formula $\begin{array}{l} CH_2{=}C - CO_2H \\ \quad\quad\quad\



Aconitic acid, $[C_6H_6O_6 (= C_3H_3(CO_2H)_3)]$. — Aconitic acid is the only tri-basic acid of this group that need be mentioned. As has been stated, it is formed when citric acid is heated to 175°. It is found in nature in aconite root, and in the sap of sugar-cane and of the beet.

Nascent hydrogen converts it into tri-carballylic acid, $C_3H_5(CO_2H)_3$. The relation between citric and aconitic acid is shown above.

Acetylene and its Derivatives.

The principal reactions by means of which it is possible to pass from a hydrocarbon of the paraffin series to the corresponding hydrocarbon of the ethylene series consist in introducing a halogen into the paraffin, and then treating the mono-halogen substitution-product with alcoholic caustic potash: —

$$C_2H_5Br = C_2H_4 + HBr.$$

The effect of these two reactions is the abstraction of two hydrogen atoms from the paraffin. The following questions therefore suggest themselves: —

Suppose a dibrom substitution-product of a paraffin be heated with alcoholic caustic potash; will the effect be that represented by the equation

$$C_2H_4Br_2 = C_2H_2 + 2\,HBr\,?$$

And, further, suppose a mono substitution-product of an ethylene hydrocarbon be treated with alcoholic potash; will the effect be that represented by the equation

$$C_2H_3Br = C_2H_2 + HBr\,?$$

If so, it is plain that we have it in our power to make a new series of hydrocarbons, the members of which must bear to the ethylene hydrocarbons the same relation that the latter bear to the paraffins. The general formula of this series would be C_nH_{2n-2}, that of the ethylene series being C_nH_{2n}, and that of the paraffin series, C_nH_{2n+2}.

A few members of the hydrocarbon series, C_nH_{2n-2}, are known, though only one is well known, and this one alone need be considered.

Acetylene (Ethine), C_2H_2. — Acetylene is contained in coal gas in small quantity. It is formed by direct combination of hydrogen and carbon when a current of hydrogen is passed between carbon poles which are incandescent in consequence of the passage of an electric current; when alcohol, ether, methane, and other organic substances are passed through a tube heated to redness; when coal gas and some other substances are burned in an insufficient supply of air, as when a Bunsen burner "strikes back"; and when ethylene bromide is treated with alcoholic caustic potash: —

$$C_2H_4Br_2 = C_2H_2 + 2\,HBr.$$

It is formed further when bromoform, $CHBr_3$, or iodoform, CHI_3, is treated with silver or zinc dust.

It is easily made by the action of water on calcium carbide: —

$$C_2Ca + 2\,H_2O = C_2H_2 + Ca(OH)_2.$$

This process is extensively used on the large scale for the preparation of acetylene for illuminating purposes.

Experiment 53. — In a Woulff's flask or an ordinary Florence flask provided with a dropping funnel and an outlet tube, put a few pieces of

calcium carbide about the size of half-inch cubes. When the water from the funnel is allowed to drop on the carbide the gas is given off at once, and the rapidity of the current can be regulated by regulating the dropping of the water. After the operation has been in progress long enough to drive the air out of the apparatus, connect a burner with the delivery tube at *A*, and set fire to the gas. Unless the burner is an "acetylene burner" the flame gives a great deal of soot and it should not be allowed to burn long. In the test-tube *B* is a strong solution of ammoniacal cuprous chloride prepared as follows: Make a saturated solution of 1 part common salt and $2\frac{1}{8}$ parts crystallized copper sulphate. Saturate with sulphur dioxide. Filter, and wash with acetic acid. Dissolve the white

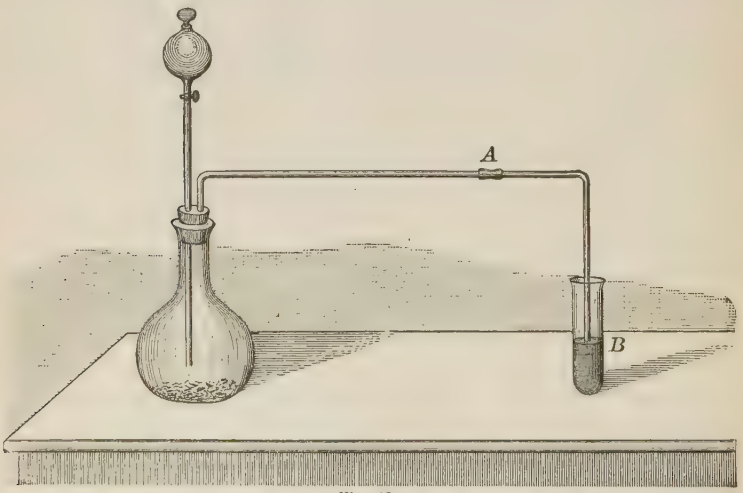


Fig. 13.

cuprous chloride in ammonia. Pass some of the gas through this solution. The acetylene will be absorbed by the copper solution, and a precipitate formed (see Exp. 54).

Acetylene is a colorless gas of an unpleasant odor, resembling that of the leek. It burns with a luminous, sooty flame.

When heated to a sufficiently high temperature, it is converted into the polymeric substances, benzene, C_6H_6, and styrene, C_8H_8. It unites with hydrogen to form ethylene and

ethane. It unites with nitrogen, under the influence of the sparks from an induction coil, forming hydrocyanic acid: —

$$C_2H_2 + 2\,N = 2\,HCN.$$

Acetylene forms some curious compounds with metals and metallic oxides. Among them may be mentioned the copper compound obtained in Exp. 53. This has the composition C_2Cu_2, which is the cuprous salt of acetylene. It is a reddish-brown substance, insoluble in water. When dry, it explodes violently at 120°. Hydrochloric acid decomposes it, acetylene being evolved.

Experiment 54. Filter off the precipitate obtained in Exp. 53, and wash it until the wash-water runs through colorless. Bring the precipitate, together with a little water, into a flask furnished with a funnel-tube and a delivery-tube. Slowly add concentrated hydrochloric acid, and notice the evolution of gas. Collect some of it in a small cylinder over water, and burn it.

Acetylene acts like a weak dibasic acid. Cuprous carbide, C_2Cu_2, calcium carbide, C_2Ca, silver carbide, C_2Ag_2, etc., are salts of the acid.

Acetylene unites with bromine, forming the compound $C_2H_2Br_4$, tetra-brom-ethane. It unites with hydrobromic and hydriodic acids, forming substitution-products of the saturated hydrocarbons: —

$$C_2H_2 + 2\,HI = C_2H_4I_2.$$

The union between the carbon atoms in acetylene is commonly represented by three lines ($\equiv$), or three dots ($\vdots$). Thus acetylene is written $\begin{matrix} CH \\ \vdots \\ CH \end{matrix}$ or $CH \vdots CH$. Like the sign of the ethylene condition the sign of the acetylene condition should not be interpreted too literally. It is best to regard it as the sign of the condition illustrated by acetylene. *This condition carries with it the power to take up four atoms of a halogen, or two molecules of hydrobromic acid and similar acids, and to form metallic derivatives like those of acetylene above referred to.*

Most of the higher members of the acetylene series of hydrocarbons bear to acetylene the same relation that the higher members of the ethylene series bear to ethylene. The first one is

Allylene or *methyl-acetylene* . . . . $\begin{matrix} C.CH_3 \\ \vert\vert\vert \\ CH \end{matrix}$;

the second is

Ethyl-acetylene . . . . . $\begin{matrix} C.C_2H_5 \\ \vert\vert\vert \\ CH \end{matrix}$,

or *Dimethyl-acetylene* . . . . . $\begin{matrix} C.CH_3 \\ \vert\vert\vert \\ C.CH_3 \end{matrix}$.

It should be noticed in this connection that there is a hydrocarbon of the formula C_4H_6, which, strictly speaking, is not a homologue of acetylene, though it is very closely allied to dimethyl-acetylene. It has the formula $\begin{matrix} CH=CH_2 \\ \vert \\ CH=CH_2 \end{matrix}$.

The homologues of acetylene may be divided into two classes:

1. Those which are obtained from acetylene by the replacement of one or both the hydrogen atoms by saturated radicals, such as methyl, ethyl, etc. These are called the *true homologues.* They all retain the condition peculiar to acetylene.

2. Those in which the ethylene condition occurs twice, as in the hydrocarbons of the formulas

$$\begin{matrix} CH=CH_2 \\ \vert \\ CH=CH_2 \end{matrix} \quad , \qquad \begin{matrix} C(CH_3)_2 \\ \Vert \\ C=CH_2 \end{matrix} \quad , \text{ etc.}$$

These may be called *diethylene derivatives.* These, like acetylene and its true homologues, have the power to take up four atoms of a halogen, or two molecules of hydrobromic acid and similar acids, but they do not form copper and silver salts.

Propargyl alcohol, C_3H_4O. — This alcohol is mentioned merely as an example of alcohols which are derived from the acetylene hydrocarbons. It is the hydroxyl derivative of

allylene, or methyl-acetylene. It is made by treating brom-allyl alcohol, $C_3H_4Br.OH$, with alcoholic caustic potash: —

$$\begin{array}{l} CH_2OH \\ | \\ CBr = CH_2 \end{array} = \begin{array}{l} CH_2OH \\ | \\ C \equiv CH \end{array} + HBr.$$

Acids, $C_nH_{2n-4}O_2$.

These acids are the carboxyl derivatives of the acetylene hydrocarbons, and hence differ from the members of the acrylic acid series by two atoms of hydrogen each, and from the members of the fatty acid series by four atoms of hydrogen each.

Propiolic acid, $C_3H_2O_2\left(\begin{array}{l} CH \\ \vert\vert\vert \\ C.CO_2H \end{array}\right)$. — The potassium salt of this acid has been made from the acid potassium salt of acetylene-dicarbonic acid, $\begin{array}{l} C.CO_2H \\ \vert\vert\vert \\ C.CO_2H \end{array}$, by heating it in water solution. Acetylene-dicarbonic acid is formed by heating dibrom-succinic acid with a water solution of caustic potash: —

$$\begin{array}{l} CHBr.CO_2H \\ | \\ CHBr.CO_2H \end{array} = \begin{array}{l} C.CO_2H \\ \vert\vert\vert \\ C.CO_2H \end{array} + 2\,HBr.$$

Tetrolic acid, $C_4H_4O_2\left(\begin{array}{l} C.CH_3 \\ \vert\vert\vert \\ C.CO_2H \end{array}\right)$, is obtained by treating β-chlor-crotonic acid with caustic potash: —

$$\begin{array}{l} CCl.CH_3 \\ \Vert \\ CH.CO_2H \end{array} = \begin{array}{l} C.CH_3 \\ \vert\vert\vert \\ C.CO_2H \end{array} + HCl.$$

Sorbic acid, $C_6H_8O_2(CH_3.CH = CH.CH = CH.CO_2H)$. — This acid occurs in the unripe berries of the mountain ash. It takes up hydrogen and yields *hydrosorbic acid,* a member of the acrylic acid series (see table, p. 233). It also takes up

bromine, the final product of the action being an acid of the formula $C_5H_7Br_4 . CO_2H$. With hydrobromic acid it forms dibrom-caproic acid: —

$$C_5H_7 . CO_2H + 2\,HBr = C_5H_9Br_2 . CO_2H.$$
Dibrom-caproic acid.

It will be observed that sorbic acid is a diethylene derivative and that it does not contain the acetylene condition.

Linoleïc acid, $C_{18}H_{32}O_2$ ($C_{17}H_{31}CO_2H$). — This acid occurs in the form of an ethereal salt of glycerol in drying oils. It can be obtained from linseed oil by saponification. It is an oily liquid, one of the most marked properties of which is its power to take up oxygen from the air, and turn into a solid substance. Linseed oil itself has this property of hardening or drying. It is the principal substance belonging to the class of *drying oils*. The oil is used extensively as a constituent of varnishes and of oil paints.

The relations between linoleïc, oleïc, and stearic acids as far as their composition is concerned are shown by the following formulas: —

$C_{18}H_{36}O_2$	$C_{18}H_{34}O_2$	$C_{18}H_{32}O_2$
Stearic acid.	Oleïc acid.	Linoleïc acid.

Valylene, C_5H_6. — We have thus far had to deal with three series of hydrocarbons of the general formulas C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-2}. We naturally inquire whether there is a series of the general formula C_nH_{2n-4}. A few members of the series have been prepared by abstracting hydrogen from certain of the acetylene hydrocarbons by the action of alcoholic potash on the bromine derivatives. Thus, *valylene*, C_5H_6, has been made by treating valerylene bromide, $C_5H_8Br_2$, with alcoholic potash: —

$$C_5H_8Br_2 = C_5H_6 + 2\,HBr.$$

It is a liquid. Its most characteristic property is its power to unite with bromine to form the saturated compound $C_5H_6Br_6$.

Dipropargyl, C_6H_6. — Dipropargyl is obtained from the compound dibrom-diallyl, $C_6H_8Br_2$, by boiling with alcoholic caustic potash: —

$$C_6H_8Br_2 = C_6H_6 + 2\,HBr.$$

It unites very readily with bromine, forming, as the final product of the action, the compound $C_6H_6Br_8$, which is an octo-bromine substitution-product of hexane, C_6H_{14}.

The unsaturated hydrocarbons and their derivatives thus far considered are obtained by simple reactions from the saturated compounds, and they all have the power to take up bromine, hydrobromic acid, etc., readily, and thus to pass back to the saturated condition. Whatever the real nature of the relation between the carbon atoms in all these unsaturated hydrocarbons may be, it certainly is easily changed to the condition that exists in the saturated compounds. There are several hydrocarbons, however, which are unsaturated but which are not easily converted into derivatives of the saturated hydrocarbons. Although under some circumstances they with difficulty unite directly with the halogens, they do not take up enough to convert them into derivatives of the paraffins; and the products formed are unstable, easily giving up the halogen atoms with which they united. The simplest hydrocarbon of this new kind is the well-known benzene, which is isomeric with dipropargyl. Before proceeding to the study of benzene and its derivatives, it will be well to inquire whether the abstraction of hydrogen by the reaction chiefly used can be pushed further than it has thus far been pushed. Can we, in other words, by means of this reaction get hydrocarbons of the formula C_nH_{2n-8} which have the power to unite directly with ten atoms of bromine? Such hydrocarbons have not been prepared. Hydrocarbons of the formula C_nH_{2n-8} are known; but they are not made from the paraffins by abstracting hydrogen, and they are not converted into substitution-

products of the paraffins by the addition of halogens and halogen acids.

The compounds which have been treated of fall under five general heads, according to the formulas of the hydrocarbons. These heads are,—

1. *Hydrocarbons,* C_nH_{2n+2}, *the paraffins and their derivatives.*
2. *Hydrocarbons,* C_nH_{2n}, *or olefins and their derivatives.*
3. *Hydrocarbons,* C_nH_{2n-2}, *or the acetylene hydrocarbons and their derivatives.*
4. *Hydrocarbons,* C_nH_{2n-4}, *and their derivatives.*
5. *Hydrocarbons,* C_nH_{2n-6}, *and their derivatives.*

This classification, while strictly correct, is misleading, inasmuch as it conveys no idea in regard to the relative importance of the compounds of the different classes. As we have seen, the only compounds whose treatment required much time are those of the first class. These compounds stand out prominently, and are distinguished by the frequency of their occurrence and their great number. The compounds of the second class are much less numerous, and but a small number of them are familiar substances. While a few substances belonging to the third class are known, our knowledge in regard to the class is much more limited than even that of the second class. Finally, as regards the fourth and fifth classes, the few representatives of them that are known are at present scientific curiosities. Thus, after we leave the paraffin derivatives, our knowledge dwindles away very rapidly when we pass to the following classes, until it ends with a single compound in the fifth class.

Let us now pass to the consideration of a new group, the importance and number of whose members entitle it to be placed side by side with the group of paraffin derivatives.

CHAPTER XIV.

THE BENZENE SERIES OF HYDROCARBONS.—AROMATIC COMPOUNDS.

The fundamental substance of this group is benzene, C_6H_6, which bears to the group the same relation that marsh gas bears to the group of paraffin derivatives. Benzene, together with some of its homologues, is a product of the distillation of bituminous coal, and is, therefore, contained in *coal tar*. As coal tar is the raw material from which all benzene derivatives are obtained, it will be well briefly to consider the conditions of its formation and the method of obtaining pure hydrocarbons from it.

Coal tar is a thick, black, tarry liquid, which is obtained in the manufacture of illuminating gas from bituminous coal. The coal is heated in retorts, and all the products passed through a series of tubes called *condensers*. These are kept cool, and in them the liquid and volatile solid products are condensed, forming together the coal tar. It is an extremely complex mixture, from which a great many substances have been obtained. Among those most readily obtained from it are the hydrocarbons of the benzene series, as well as the hydrocarbons naphthalene and anthracene, both of which are important substances.

When the tar is heated, of course the most volatile liquids pass over first. These are collected in vessels containing water. The first portions of the distillate float on water, and constitute what is called the *light oil*. After a time hydrocarbons and other substances of greater specific gravity than the light oil

pass over. These portions sink under water, and constitute the *heavy oil.*

The light oil is treated with caustic soda, which removes phenol (carbolic acid) and similar substances, and with sulphuric acid, which removes certain basic compounds and olefins. The residue is then subjected to fractional distillation, by which means the first two members of the series can be obtained in very nearly pure condition. As these hydrocarbons form the basis of a number of important industries, they are separated from coal tar on the large scale.

The principal members of the series are named in the table below.

HYDROCARBONS, C_nH_{2n-6}

BENZENE SERIES.

Benzene	C_6H_6.
Toluene	C_7H_8.
Xylene	C_8H_{10}.
Mesitylene, Pseudocumene	C_9H_{12}.
Durene, Cymene	$C_{10}H_{14}$.
Hexa-methyl benzene	$C_{12}H_{18}$.

Benzene, C_6H_6. — Benzene is prepared, as above described, from the light oil obtained from coal tar. A large part of the benzene now used is obtained from the gas formed in the coke furnaces. It is also prepared by heating benzoic acid with lime, when the acid breaks up into carbon dioxide and benzene: —

$$C_7H_6O_2 = C_6H_6 + CO_2.$$

NOTE FOR STUDENT. — What is the analogous method for the preparation of marsh gas?

Benzene has been made further by simply heating acetylene: —

$$3\,C_2H_2 = C_6H_6.$$

To purify the hydrocarbon obtained by fractional distillation from light oil, it is cooled down to a low temperature, and that which does not solidify is poured off. The crystals are pressed in the cold between layers of bibulous paper, and are then very nearly pure benzene. This can be further purified by treatment with sulphuric acid, which removes a small quantity of a substance containing sulphur, and known as *thiophene*, C_4H_4S. Perfectly pure benzene is obtained by distilling pure benzoic acid with lime.

Experiment 55. Mix intimately 50g benzoic acid and 100g quicklime, and distil from a flask connected with a condenser. See that the materials and apparatus are dry. Add a little calcium chloride to the distillate; and, after it has stood for an hour or two, redistil it from a distilling-bulb of proper size, noting the temperature at which it boils. Put the redistilled hydrocarbon in a test-tube, and surround it with a freezing mixture.

Experiment 56. In most places where there are gas-works it will not be difficult to get a quantity of light oil. The separation of some of this into benzene and toluene, and the purification of the two hydrocarbons, is the best possible introduction to a study of the aromatic compounds. The benzene and toluene thus obtained may be used in the preparation of a number of typical derivatives according to methods which will be described. In fractioning the light oil, it will be observed that there is a tendency to an accumulation of the distillates in the parts boiling near 80.5° (the boiling-point of benzene) and 110° (the boiling-point of toluene). The final purification of the benzene should be effected by freezing and pressing, as described above. The toluene should be distilled until its boiling-point is not changed by redistillation.

Benzene is a colorless liquid boiling at 80.5°. It has a peculiar, pleasant odor. Several of the homologues of benzene have a similar odor. Hence the name *aromatic compounds* was given to them originally, and it is still in general use. Benzene is lighter than water, its specific gravity being 0.899 at 0°. It is insoluble in water, soluble in alcohol and chloroform. It burns with a bright, luminous, smoky flame.

Experiment 57. Pour a layer of benzene on water in a small evaporating-dish. Set fire to it.

Benzene crystallizes in rhombic prisms when cooled to 0°. These melt at 5.4°. It is an excellent solvent for oily and resinous substances.[1]

Chemical conduct of benzene, and hypothesis regarding its structure. In the light of the knowledge we have already gained in studying hydrocarbons which contain a smaller proportion of hydrogen than the paraffins do, we should naturally expect to find that benzene can easily be converted into a derivative of hexane. We should naturally expect to find that it unites with bromine, just as dipropargyl does, to form an octo-brom-hexane thus, —

$$C_6H_6 + Br_8 = C_6H_6Br_8;$$

with hydrobromic acid to form tetra-brom-hexane thus, —

$$C_6H_6 + 4\,HBr = C_6H_{10}Br_4;$$

and probably with hydrogen to form hexane, —

$$C_6H_6 + 8\,H = C_6H_{14}.$$

But none of these reactions takes place. Hydrobromic acid, which combines so readily with all the unsaturated compounds hitherto considered, does not act at all upon benzene. Bromine acts readily enough, but the action which usually takes place is like that which takes place with the saturated paraffins. It is *substitution, and not addition.* Thus, bromine forms monobrom-benzene, C_6H_5Br, under ordinary circumstances. If, however, the action takes place in the direct sunlight, a product is formed which has the formula $C_6H_6Br_6$, known as *benzene hexabromide*, and to this no more bromine can be added.

Treated with hydriodic acid, benzene takes up six atoms of hydrogen and yields a hydrocarbon of the composition C_6H_{12}. This is not a member of the ethylene series.

[1] Benzene, the chemical individual of the definite formula C_6H_6, must not be confounded with "benzine," the commercial substance obtained in the refining of petroleum (see p. 110).

The facts mentioned show clearly that benzene differs in some way fundamentally from all the hydrocarbons which have been treated of thus far. But these facts are not sufficient to enable us to form an hypothesis in regard to its structure. On studying the many substitution-products of benzene, however, we soon become acquainted with facts of a different order and of the highest importance.

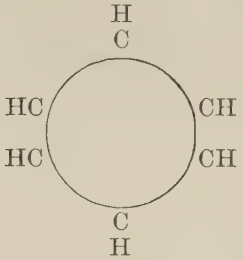
It will be remembered that the theory in regard to the relations of the paraffins to each other is based upon the fact, that only one mono-substitution product of marsh gas can be obtained with any given substituting agent. There is but one chlor-methane, but one brom-methane, etc. This fact leads to the belief that each hydrogen atom of marsh gas bears the same relation to the carbon atom, or that marsh gas is a symmetrical compound. A similar conclusion has been reached in regard to benzene; and it is based upon a most exhaustive study of the substitution-products. Notwithstanding almost innumerable efforts to prepare isomeric mono-substitution products of benzene, no such isomeric substances have been prepared. There is but one mono-brom-benzene, but one mono-chlor-benzene, etc., etc. Further, mono-brom-benzene has been prepared by substituting bromine for each of the six hydrogen atoms of benzene successively; and the product has been found to be the same, no matter which hydrogen is replaced. As this fact is of fundamental importance, it will be well to point out how it is possible to replace the six hydrogens successively, and to know that in each case a different hydrogen atom is replaced. While it would lead too far to follow this subject in detail, the principle made use of can be made clear in a few words: —

We have a compound, the formula of which is C_6H_6. Write it thus, $C_6\overset{1}{H}\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, numbering the hydrogen symbols to facilitate reference to them. The problem is to replace, say $\overset{1}{H}$, by bromine; in a second case, to replace $\overset{2}{H}$ by bromine; in a third, $\overset{3}{H}$, etc.; and to compare the six mono-brom-benzenes thus

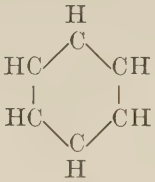
obtained. Suppose we treat benzene with bromine. We get a mono-brom-benzene, and we know that one of the hydrogen atoms is replaced by bromine, but of course we cannot tell which one. We may assume that it is any one of the six represented in the above formula. For the sake of the argument, call it $\overset{1}{H}$. Our compound is therefore $C_6Br\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}H$. Now treat this compound with something else which has the power to replace the hydrogen, say nitric acid. A second hydrogen atom is replaced by the nitro group NO_2. Again, we do not know which one of the hydrogen atoms is replaced in this operation, *but we do know that it is a different one from that which was replaced by the bromine in the first operation.* Call it $\overset{2}{H}$. We have, therefore, the compound $C_6Br(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}H$. By treating this compound with nascent hydrogen, two reactions take place, the chief one for our present purpose being the replacement of the bromine by hydrogen. In other words, $\overset{1}{H}$ is put back into the compound again, and we have $C_6\overset{1}{H}(NH_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}H$. By means of two reactions which will be studied farther on it is a simple matter to replace the amino group by bromine. This done, we have the compound $C_6\overset{1}{H}Br\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}H$, or a mono-brom-benzene, in which the bromine certainly replaces a different hydrogen atom from that replaced by direct substitution. The two products are, however, identical. The above explanation will serve to make clear the principle that is involved in the study of the relations which the hydrogen atoms contained in benzene bear to the molecule. The principle has been applied successively to all the hydrogen atoms, and, as already stated, the result is the proof that all these hydrogen atoms bear the same relation to the molecule. The same is true of the carbon atoms, as the compound is symmetrical.

How can we imagine six carbon atoms and six hydrogen atoms arranged so that all these shall bear the same relation

to the molecule? The simplest conception is that each carbon is in combination with one hydrogen, and that the six carbon atoms are arranged in the form of a ring, and not, as in the paraffins, in the form of an open chain, or a chain with branches. Using our ordinary method of representation, this conception is symbolized in the formula

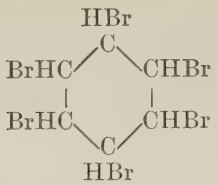


or, as the curved lines have no special significance, the expression becomes



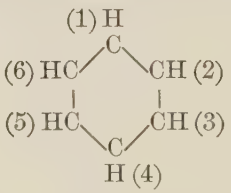
This symbol, then, is the expression of a thought suggested by a study of the chemical conduct of benzene. Before we can accept it as probable, it must first be tested by all the facts known to us. If it is not in accordance with all of them, if it suggests possibilities which are not realized, then it must be discarded.

In the first place, then, does it account for the addition products, benzene hexabromide, hexa-hydro-benzene, etc.? The formula represents each carbon atom as trivalent, and we should expect, therefore, that each one could take up an additional univalent atom, forming, in the case of bromine, a compound of the formula

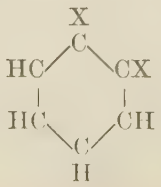


in which each carbon atom is acting as a quadrivalent atom. Unless the ring form of combination between the carbon atoms is broken up, it is impossible for the compound to take up more bromine. Hence, the last product of the addition of bromine to benzene should be benzene hexabromide. The facts and the hypothesis are in harmony.

Again, we may inquire: Of how many isomeric di-substitution products of benzene does the hypothesis suggest the existence? Numbering the hydrogens in the formula, we have: —

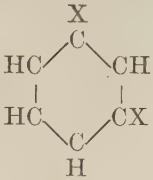


The hydrogens (1) and (2), (2) and (3), (3) and (4), (4) and (5), (5) and (6), and (6) and (1), bear the same relations to each other; and, according to the formula, whether we replace (1) and (2), or (2) and (3), or (3) and (4), or any other of the above-named pairs, the product ought to be the same. We should get a compound of which the following is the general expression, in which X represents any substituting atom or group: —



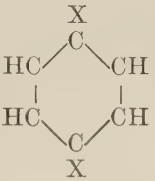
Formula I.

In the second place, the hydrogens (1) and (3), (2) and (4), (3) and (5), (4) and (6), (5) and (1), and (6) and (2) bear to each other the same relation, but a different relation from that which the above pairs do. Replacing any such pair, we should have a second compound, which is represented by the general formula



Formula II.

Finally, there is a third kind of relation, which is that between hydrogens (1) and (4), (2) and (5), and (3) and (6); and, by replacing such a pair, we should get a compound represented by the general formula



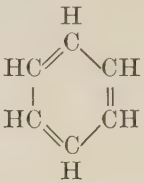
Formula III.

The hypothesis suggests no other possibilities. We see thus that the hypothesis indicates the existence of three, and only three, classes of di-substitution products of benzene. There ought to be three, and only three, di-chlor-benzenes; three, and only three, di-brom-benzenes, etc.

The di-substitution products have been studied very exhaustively for the purpose of determining definitely whether the conclusion above reached is in accordance with the facts; and it may be said at once, that every fact thus far discovered is in harmony with the hypothesis. Three well-marked classes of isomeric di-substitution products of benzene are known, and only three; and many representatives of the three classes have

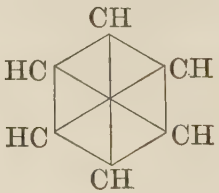
been studied carefully. There are many other facts of less importance known which furnish arguments in favor of the benzene hypothesis expressed in the formula above discussed, but this is not the place to discuss them. Let it suffice, for the present, to recognize that the hypothesis is in accordance with the most important facts known to us.

There is one point that has not been touched upon, and that is the relation of the carbon atoms to each other. The formula is commonly written thus: —

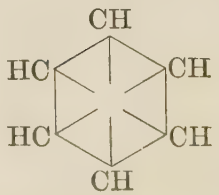


which indicates that the carbon atoms are joined together alternately by single and by double bonds. This formula, however, expresses something about which we know little, and concerning which it is difficult, at present, to form any conception.

Another formula that has been suggested is this: —



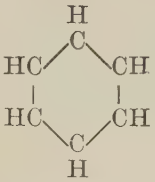
Still another is: —



In each of these, as will be seen, an attempt is made to account

for the fourth bond of each carbon atom. The question involved is an extremely difficult one to investigate, and it is not surprising that chemists do not agree as to the formula to be preferred.

The simple formula



leaves the question as to the relation between the carbon atoms entirely open, and suffices for most purposes.

The benzene hypothesis has been treated of somewhat fully, for the reasons, that it has played an extremely important part in the study of the benzene derivatives, and that its use serves greatly to simplify the study of these derivatives.

Benzene and its homologues form nitro compounds and sulphonic acids by direct treatment with nitric and sulphuric acids, respectively. This distinguishes them from the paraffins and other hydrocarbons hitherto treated of.

Toluene, $C_7H_8 (= C_6H_5 . CH_3)$. — Toluene was known before it was obtained from coal tar, as it is formed by the dry distillation of Tolu balsam, whence its name. Its relation to benzene is shown by its synthesis from brom-benzene and methyl iodide: —

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5 . CH_3 + NaBr + NaI.$$

Note for Student. — Compare this reaction with that used in the synthesis of ethane from methane, of propane from ethane and methane, etc.

According to this synthesis, toluene appears as *methyl-benzene*, or benzene in which one hydrogen is replaced by methyl; or as *phenyl-methane*, or methane in which one hydrogen atom is replaced by the radical phenyl, C_6H_5, which bears the same relation to benzene that methyl bears to marsh gas.

Toluene is a colorless liquid which boils at 110°; has the specific gravity 0.8824 at 0°; and has a pleasant aromatic odor.

It is very susceptible to the action of reagents yielding a large number of substitution-products, some of the most important of which will be taken up farther on.

But one toluene or methyl-benzene has ever been discovered.

Towards oxidizing agents its conduct is peculiar and interesting. The methyl is oxidized, while the phenyl remains intact. The product is a well-known acid, benzoic acid, which, as we have seen, breaks up readily into carbon dioxide and benzene. It has the composition $C_7H_6O_2$, and is the carboxyl derivative of benzene, $C_6H_5.CO_2H$. The oxidation of toluene is represented by the equation

$$C_6H_5.CH_3 + 3\,O = C_6H_5.CO_2H + H_2O.$$

Xylenes, C_8H_{10}[$= C_6H_4(CH_3)_2$]. — That portion of light oil which boils at about 140° was originally called *xylene*. It was afterwards found that this coal-tar xylene consists of three isomeric hydrocarbons. As the boiling-points of these three substances lie quite near together, it is impossible to separate them by means of fractional distillation. By treatment with sulphuric acid, however, they can be separated, and thus obtained in pure condition. They are known as *ortho-xylene*, *meta-xylene*, and *para-xylene*.

Ortho-xylene resembles benzene and toluene in its general properties, but boils at 140° to 141°.

Meta-xylene boils at 137°.

Para-xylene boils at 136° to 137°.

These hydrocarbons have also been obtained from toluene by

means of the reaction made use of for the purpose of converting benzene into toluene: —

$$C_6H_4 < \begin{matrix} CH_3 \\ Br \end{matrix} + CH_3I + 2\,Na = C_6H_4 < \begin{matrix} CH_3 \\ CH_3 \end{matrix} + NaBr + NaI.$$

This shows that they are all *methyl-toluenes.* There are three mono-brom-toluenes, known as ortho-, meta-, and para-brom-toluene. For the preparation of ortho-xylene, ortho-brom-toluene is used; meta-brom-toluene yields meta-xylene, and para-brom-toluene yields para-xylene.

Ortho- and meta-xylene have also been obtained from certain acids, which bear to them the same relation that benzoic acid bears to benzene: —

$$C_6H_3 \left\{ \begin{matrix} CH_3 \\ CH_3 \\ CO_2H \end{matrix} \right. = C_6H_4(CH_3)_2 + CO_2.$$

The reaction by which *meta-xylene* is formed from *mesitylenic acid* is of special importance, as will be pointed out.

By oxidation, the xylenes undergo changes like that which is illustrated in the formation of benzoic acid from toluene, and which consists in the transformation of methyl into carboxyl. The first change gives acids of the formula $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix}$, one corresponding to each xylene. By further oxidation, these three monobasic acids are converted into dibasic acids of the formula $C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$. Thus, we have the three reactions, all of the same kind: —

$$(1)\ C_6H_5.CH_3 + 3\,O = C_6H_5.CO_2H + H_2O;$$

$$(2)\ C_6H_4 < \begin{matrix} CH_3 \\ CH_3 \end{matrix} + 3\,O = C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix} + H_2O;$$

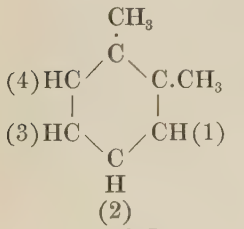
and $$(3)\ C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix} + 3\,O = C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} + H_2O.$$

The three monobasic acids of the formula $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix}$ are known as *ortho-toluic*, *meta-toluic*, and *para-toluic* acids respectively; and the three dibasic acids obtained from them are known as *ortho-phthalic*, *meta-phthalic*, and *para-phthalic* acids. Starting thus from the three brom-toluenes, we get, first, three xylenes, then three toluic acids, and finally three phthalic acids. In each case, we distinguish between the three isomeric compounds by the prefixes *ortho*, *meta*, and *para*. In a similar way, all di-substitution products of benzene are designated. We therefore have three series into which all di-substitution products of benzene can be arranged; and these are known as the *Ortho-series*, the *Meta-series*, and the *Para-series*. In arranging them in this way, we may select any prominent di-substitution product, and call it an *ortho compound;* and then call one of its isomerides a *meta compound*, and the other a *para compound*. Having thus a representative of each of the three classes, the remainder of the problem consists in determining for each di-substitution product, by means of appropriate reactions, into which one of the three representatives it can be transformed. If from a given compound we get the representative of the ortho series, we conclude that the compound belongs to the ortho series; if we get the representative of the meta series, we conclude that the compound is a meta compound; and if we get the representative of the para series, we conclude that the compound is a para compound. As representatives, we may select either the three xylenes or the three phthalic acids. Now, to repeat, any di-substitution product of benzene which can be converted into ortho-xylene or into ortho-phthalic acid is regarded as an ortho compound, etc.

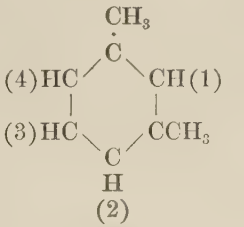
This classification of the di-substitution products of benzene into the ortho, meta, and para series, by means of chemical transformations, is entirely independent of any hypothesis re-

garding the nature of benzene. We may now ask, however, which one of the three general expressions given above (see formulas I., II., and III., pp. 256, 257) represents the relation of the groups in the ortho compounds, which one the relation in the meta compounds, and which one the relation in the para compounds. If we can answer these questions for any three isomeric di-substitution products, the answer for the rest will follow. To reduce the problem to simple terms, therefore, let us take the three xylenes. We have three xylenes and three formulas: how can we determine which particular formula to assign to each xylene?

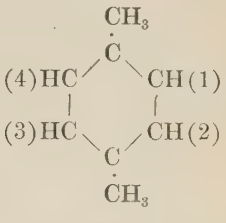
As may be imagined, this determination is by no means a simple matter; and it has been the occasion of a great many investigations. Theoretically, the simplest method available consists in carefully studying the substitution-products of each xylene, to discover how many varieties of mono-substitution products can be obtained from each. The formulas are: —



Formula I.



Formula II.

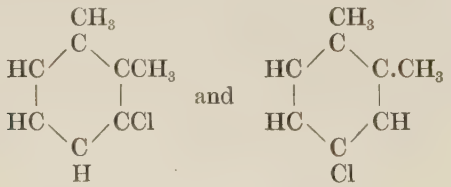


Formula III.

Each of the four unreplaced benzene hydrogens of the xylene of formula III. bears the same relation to the molecule. It therefore should make no difference which one is replaced, the product ought to be the same. This should not be true of the xylenes represented by formulas I. and II. That xylene, whose structure is represented by formula III., ought therefore to yield but one kind of mono-substitution product. On studying the xylenes, we find the one which boils at 136° to 137°,

called para-xylene, yields but one kind of mono-substitution products; that is, we can get from it only one mono-brom-xylene; only one mono-nitro-xylene, etc. We therefore conclude that para-xylene is represented by formula III. above; and, further, that formula III., on p. 257, is the general expression for all para compounds.

Examining formula I., on the preceding page, in the same way, we see that H(1) and H(4) bear the same relation to the molecule; and that H(3) and H(2) also bear the same relation to the molecule, though different from that of H(1) and H(4). Two chlor-xylenes of the formulas



ought to be obtainable from the xylene of formula I.

In the same way three mono-substitution products should be obtainable from the xylene of formula II. The method, the principle of which is thus indicated briefly, while theoretically simple enough, is very difficult in its application, except in the case of the para compounds. Other methods have therefore been used, and these will be discussed under mesitylene and naphthalene. It may be said, in anticipation, that the result of all observations point to formula I. for ortho-xylene; to formula II. for meta-xylene, and to formula III. for para-xylene.

Ethyl-benzene, $C_8H_{10}(= C_6H_5.C_2H_5)$. — This hydrocarbon is isomeric with the xylenes, but differs from them in that it contains an ethyl group in the place of one hydrogen of benzene,

instead of two methyl groups in the place of two hydrogens of benzene. It is made by treating a mixture of brom-benzene and ethyl bromide with sodium: —

$$C_6H_5Br + C_2H_5Br + 2\,Na = C_6H_5 . C_2H_5 + 2\,NaBr.$$

Its conduct towards oxidizing agents distinguishes it from the xylenes. It yields benzoic acid, just as toluene does. In this case, as in that of toluene, the paraffin radical is converted into carboxyl. It has been found that no matter what this radical may be, it is, under the same circumstances, converted into carboxyl. Thus, the conversions indicated below take place: —

$C_6H_5 . CH_3$ gives $C_6H_5 . CO_2H$.
$C_6H_5 . C_2H_5$ " $C_6H_5 . CO_2H$.
$C_6H_5 . C_3H_7$ " $C_6H_5 . CO_2H$.
$C_6H_5 . C_5H_{11}$ " $C_6H_5 . CO_2H$.
$C_6H_4 < \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}$ " $C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$.
$C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix}$ " $C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$, etc., etc.

Mesitylene, C_9H_{12} [$= C_6H_3(CH_3)_3$]. — Mesitylene is contained in small quantity in light oil, and can be obtained in pure condition from this source. It is most readily prepared by treating acetone with sulphuric acid: —

$$3\,C_3H_6O = C_9H_{12} + 3\,H_2O.$$

It can also be made by treating methyl-acetylene, $CH_3.C \equiv CH$, with sulphuric acid, the action in this case being perfectly analogous to the polymerisation of acetylene: —

$$3\,CH \equiv CH = C_6H_6;$$
$$3\,CH_3 . C \equiv CH = C_6H_3(CH_3)_3.$$

It is a liquid resembling the lower members of the series in its general properties. It boils at 163°.

Its conduct towards oxidizing agents shows that it is a *trimethyl-benzene*. When boiled with dilute nitric acid, it yields *mesitylenic acid*, $C_9H_{10}O_2$, and *uvitic acid*, $C_9H_8O_4$; and, by

further oxidation with chromic acid, *trimesitic acid*, $C_9H_6O_6$, is formed. By distillation with lime, mesitylenic acid yields meta-xylene and carbon dioxide; uvitic acid yields toluene and carbon dioxide; and *trimesitic acid* yields benzene and carbon dioxide. The formation and decomposition of the acids may be represented by the equations following: —

$$\underset{\text{Mesitylene.}}{C_6H_3(CH_3)_3} + 3\,O = \underset{\text{Mesitylenic acid.}}{C_6H_3\begin{cases}CH_3\\CH_3\\CO_2H\end{cases}} + H_2O;$$

$$\underset{\text{Mesitylenic acid.}}{C_6H_3\begin{cases}CH_3\\CH_3\\CO_2H\end{cases}} + 3\,O = \underset{\text{Uvitic acid.}}{C_6H_3\begin{cases}CH_3\\CO_2H\\CO_2H\end{cases}} + H_2O;$$

$$\underset{\text{Uvitic acid.}}{C_6H_3\begin{cases}CH_3\\CO_2H\\CO_2H\end{cases}} + 3\,O = \underset{\text{Trimesitic acid.}}{C_6H_3\begin{cases}CO_2H\\CO_2H\\CO_2H\end{cases}} + H_2O;$$

$$\underset{\text{Mesitylenic acid.}}{C_6H_3\begin{cases}CH_3\\CH_3\\CO_2H\end{cases}} = \underset{\text{Meta-xylene.}}{C_6H_4\begin{cases}CH_3\\CH_3\end{cases}} + CO_2;$$

$$\underset{\text{Uvitic acid.}}{C_6H_3\begin{cases}CH_3\\CO_2H\\CO_2H\end{cases}} = \underset{\text{Toluene.}}{C_6H_5.CH_3} + 2\,CO_2;$$

$$\underset{\text{Trimesitic acid.}}{C_6H_3\begin{cases}CO_2H\\CO_2H\\CO_2H\end{cases}} = \underset{\text{Benzene.}}{C_6H_6} + 3\,CO_2.$$

These transformations show clearly that mesitylene is trimethyl-benzene, but they do not show in what relation the methyl groups stand to each other.

An ingenious speculation in regard to this relation is based upon the fact that mesitylene is formed from acetone. It

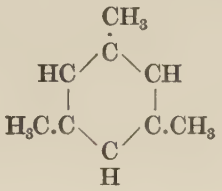
appears probable that each of the three molecules of acetone taking part in the reaction,

$$3\,C_3H_6O = C_9H_{12} + 3\,H_2O,$$

undergoes the same change. As the product contains three methyl groups, the simplest assumption that can be made is that each acetone molecule gives up water as represented thus: —

$$\underset{\text{Acetone.}}{CH_3-CO-CH_3} = CH_3-C-CH + H_2O.$$

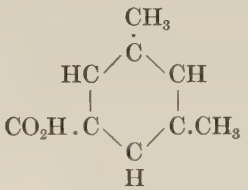
We thus have three residues, CH_3-C-CH, and these unite to form trimethyl benzene. The only way in which the union can be represented, assuming that all three act in the same way, is this: —



According to this reasoning, mesitylene is a symmetrical compound, — that is to say, each of the three methyl groups bears the same relation to the molecule; and the same is true of each of the three benzene-hydrogen atoms.

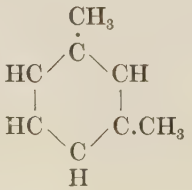
This view has been tested by replacing the three hydrogen atoms successively by bromine; and it has been found that the view is confirmed, as but one mono-bromine substitution-product of mesitylene has ever been obtained. Accepting the formula above given for mesitylene, an important conclusion follows regarding the nature of meta-xylene. For we have seen that, by oxidizing mesitylene, we get, as the first product, mesitylenic acid, — which is mesitylene, one of whose methyls has been converted into carboxyl. As all the methyl groups

bear the same relation to the molecule, it makes no difference which one is oxidized. The acid has the formula



Now, by distilling this acid with lime, carbon dioxide is given off, and meta-xylene is produced.

As the change consists in removing the carboxyl, and replacing it by hydrogen, it follows that meta-xylene must be represented by the formula

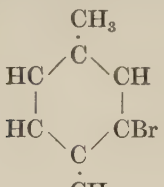


and consequently that, in all meta compounds, the two substituting atoms or groups bear to each other the relation which the two methyl groups bear to each other in this formula for meta-xylene.

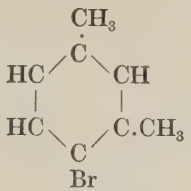
Pseudocumene, $C_9H_{12}[= C_6H_3(CH_3)_3]$. — This hydrocarbon, which is isomeric with mesitylene, occurs in coal-tar oil, from which it can be made in pure condition. Its properties are similar to those of the lower members of the series. It boils at 169.8°.

Pseudocumene has been made synthetically from brom-para-xylene and methyl iodide, and also from brom-meta-xylene and

methyl iodide. How this is possible, will be understood by an examination of the formulas below: —

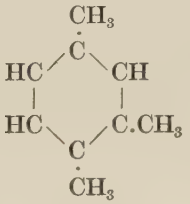


Brom-para-xylene.



Brom-meta-xylene.

Replacing the bromine by methyl, in either of the compounds represented, the product would have the formula



which is that of pseudocumene.

Cymene, Para-methyl-isopropyl-benzene, $\left.\begin{matrix}\\ \\ \end{matrix}\right\} C_{10}H_{14}\left(C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix}\right)$.

This hydrocarbon is of special importance and interest, on account of its close connection with two well-known groups of natural substances, — the groups of which camphor and oil of turpentine are the best-known representatives. It occurs in the oil of caraway and the oil of thyme. The terpenes, which are hydrocarbons of the formula $C_{10}H_{16}$, and of which oil of turpentine is the best known, easily give up two hydrogen atoms and yield cymene. Probably the simplest way to prepare cymene is to treat camphor with phosphorus pentasulphide, zinc chloride, or phosphorus pentoxide.

It is a liquid of a pleasant odor. It boils at 175°.

It has been made synthetically from para-brom-toluene and isopropyl bromide:—

$$C_6H_4 < \begin{matrix} CH_3 \\ Br \end{matrix} + C_3H_7Br + 2\,Na$$

$$= C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} + 2\,NaBr,$$

which clearly shows its relation to benzene. As the final product of its oxidation, it yields para-phthalic (terephthalic) acid:—

$$C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} \quad \text{gives} \quad C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix};$$

see p. 265.

Hexahydrobenzenes, Naphthenes.

Caucasian petroleum consists principally of a mixture of hydrocarbons that have been found to be hydrogen addition-products of members of the benzene series. They are oils that can be converted into members of the benzene series by passing them through tubes heated to a red heat. They do not react with concentrated nitric or sulphuric acid, and in this respect they differ markedly from the benzene hydrocarbons. They are called *naphthenes*.

Hexamethylene, hexanaphthene, $CH_2 < \begin{matrix} CH_2 . CH_2 \\ CH_2 . CH_2 \end{matrix} > CH_2$. —This is found not only in Caucasian petroleum but in the petroleum from other sources. American petroleum contains it in small quantity. It can be made artificially by reducing iodo-cyclohexane, $IHC < \begin{matrix} CH_2 . CH_2 \\ CH_2 . CH_2 \end{matrix} > CH_2$. It is not formed by reducing benzene. The product formed when benzene is treated with concentrated hydriodic acid is methyl-pentamethylene,

$$CH_3 . CH < \begin{matrix} CH_2 . CH_2 \\ \quad\quad | \quad\quad . \\ CH_2 . CH_2 \end{matrix}$$

Other hydrocarbons of this series are *hexahydrotoluene* or *heptanaphthene*, $CH_3 . CH < \begin{matrix} CH_2 . CH_2 \\ CH_2 . CH_2 \end{matrix} > CH_2$, hexahydroxylene or octonaphthene, $(CH_3)_2C_6H_{10}$, etc.

Tetrahydrobenzenes.

The simplest hydrocarbon of this group is *tetrahydrobenzene*, $\begin{matrix} CH_2 . CH_2 . CH \\ | \qquad\quad || \\ CH_2 . CH_2 . CH \end{matrix}$. It is formed from brom-cyclohexane by eliminating hydrobromic acid from it.

Tetrahydrotoluene, $CH_3 . C_6H_8$, is contained in the essence of resin.

Hydrocarbons, $C_{10}H_{18}$. — There are several hydrocarbons of the formula $C_{10}H_{18}$ known that belong to the series of tetrahydrobenzenes. Among them the following may be mentioned: —

Hydrocamphene. — This is obtained, together with camphene, from oil of turpentine by treating the hydrochloride of oil of turpentine with sodium.

Menthene, $CH_3 . CH < \begin{matrix} CH_2 . CH \\ CH_2 . CH_2 \end{matrix} > C . C_3H_7$. — This is formed from menthol, $C_{10}H_{20}O$, by treating it with sulphuric acid, phosphorus pentoxide, or anhydrous copper sulphate.

Dihydrobenzenes.

A number of the members of this group have been made, as, for example, dihydrobenzene, C_6H_8, dihydrotoluene, C_7H_{10}, dihydroxylenes, C_8H_{12}, etc.

Dihydro-o-xylene, or *cantharene*, $(CH_3)_2C_6H_6$, is formed by heating cantharic acid, $C_{10}H_{12}O_4$, with lime.

CHAPTER XV.

DERIVATIVES OF THE HYDROCARBONS, C_nH_{2n-6}, OF THE BENZENE SERIES.

Recalling what has been learned under the head of Derivatives of the Paraffins, we should naturally look for representatives of all the classes of compounds there met with. The derivatives of the paraffins were classified as: —

1. Halogen derivatives.
2. Oxygen derivatives, including the Alcohols, Aldehydes, Acids, etc.
3. Sulphur derivatives, including the Mercaptans, Sulphonic Acids, etc.
4. Nitrogen derivatives, including Cyanides, Amines, Nitro compounds, etc.
5. Metallic derivatives.

The derivatives of the benzene hydrocarbons may be classified in the same way, but a change in the order of treatment will be somewhat more convenient, owing to many points of analogy that exist between the halogen substitution-products, the nitro compounds, and the sulphonic acids. All of these three classes of derivatives of the benzene hydrocarbons are made by direct treatment of the hydrocarbons with the substituting agents, and in some respects resemble one another, so that they will be studied in connection. As the amino derivatives of this series are made almost exclusively from the nitro compounds by reduction, they will be taken up in connection with the nitro compounds; and, further, by treatment of the amino compounds with nitrous acid, a new class

of nitrogen derivatives, known as *diazo compounds*, not met with in connection with the paraffins, is formed. These will be taken up after the amino compounds.

After these classes have been studied, the *oxygen derivatives*, which include the phenols or simple hydroxyl derivatives of the hydrocarbons, the alcohols, aldehydes, acids, and ketones will be taken up in turn; and, finally, the *hydroxy-acids*, which are strictly analogous to the hydroxy-acids of the paraffin series.

There are thus the following classes: —

1. *Halogen derivatives.*
2. *Nitro compounds.*
3. *Amino compounds.*
4. *Diazo compounds.*
5. *Sulphonic acids.*
6. *Phenols.*
7. *Alcohols.*
8. *Aldehydes.*
9. *Acids.*
10. *Ketones* (and *Quinones*).
11. *Hydroxy-acids.*

The relations of most of these classes to the hydrocarbons are the same as those of the corresponding derivatives of the paraffin series to the paraffins; and the general methods of preparation, as well as the reactions, are the same. Hence, most of the knowledge acquired in the first part of the course may be applied to the series now under consideration.

An enormous number of derivatives of the benzene hydrocarbons have been prepared and studied; but only very few need to be studied in order to make the chemistry of all of them clear. In the following a few of the more important representatives of each class will be presented, mainly with the object of illustrating general facts and general relations.

Halogen Derivatives of Benzene.

Very little need be said in regard to these derivatives. By direct action of bromine or chlorine upon benzene the hydrogen atoms are replaced one after another, until, as the final products, *hexa-chlor-benzene*, C_6Cl_6, and *hexa-brom-benzene*, C_6Br_6, are obtained. When the action takes place in direct sunlight, addition-products, $C_6H_6Cl_6$ and $C_6H_6Br_6$, are formed. Benzene

hexachloride, $C_6H_6Cl_6$, is formed also when chlorine is conducted into boiling benzene. The addition-products are decomposed, yielding tri-substitution products of benzene and halogen acid: —

$$C_6H_6Br_6 = C_6H_3Br_3 + 3\,HBr.$$

The substitution-products are very stable. They are, as a rule, formed more easily than the halogen derivatives of the paraffins, and, as a rule, they do not give up the halogens as readily. Thus, while it is possible in the paraffin derivatives to replace chlorine and bromine by hydroxyl, the amino group, etc., these replacements cannot easily be effected in the benzene derivatives. The halogens can be removed by sodium, as shown in the synthesis of hydrocarbons: —

$$C_6H_5Br + CH_3I + 2\,Na$$
$$= C_6H_5 . CH_3 + NaBr + NaI, \text{ etc., etc.}$$

They can also be removed by nascent hydrogen, the hydrocarbons being regenerated: —

$$C_6H_4Cl_2 + 4\,H = C_6H_6 + 2\,HCl.$$

This kind of reverse substitution is not, however, effected easily.

Chlor-benzene, C_6H_5Cl. — Chlor-benzene can be made by treating benzene with chlorine, but the action is slow. The action is much hastened by adding a little iodine or ferric chloride. These substances act as *carriers*, and are found practically unchanged at the end of the operation. Chlor-benzene can also be made by boiling a diazonium salt (which see) with hydrochloric acid: —

$$C_6H_5N_2Cl + HCl = C_6H_5Cl + N_2 + HCl.$$

Brom-benzene, C_6H_5Br. — This is made by the same methods as those used in making chlor-benzene.

Iodo-benzene, C_6H_5I. — This can be made by treating benzene with iodine and iodic acid: —

$$5\,C_6H_6 + 4\,I + HIO_3 = 5\,C_6H_5I + 3\,H_2O;$$

but it is most easily made through the diazonium salt. It is a liquid that solidifies at $-30°$.

Phenyliodoso chloride, $C_6H_5 \cdot ICl_2$. — This compound is formed when iodo-benzene in chloroform solution is treated with chlorine. When it is treated with caustic potash it is converted into **iodoso-benzene, C_6H_5IO.** This has basic properties, and forms salts that are derived from the hypothetical base, $C_6H_5I(OH)_2$, as, for example, $C_6H_5I(O \cdot CO \cdot CH_3)_2$.

Iodoxy-benzene, $C_6H_5IO_2$, is formed from iodoso-benzene, either by heating it alone or by boiling its water solution: —

$$2\,C_6H_5IO = C_6H_5I + C_6H_5IO_2.$$

Diphenyliodonium Hydroxide, $(C_6H_5)_2I \cdot OH$. — This remarkable substance is formed when a mixture of iodoso- and iodoxy-benzene is shaken with silver oxide and water: —

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I \cdot OH + AgIO_3.$$

It is strongly alkaline and forms salts that have many points of resemblance with the salts of thallium.

Diphenyliodonium hydroxide may be regarded as the diphenyl derivative of a hypothetical base, iodonium hydroxide, $H_2I(OH)$, that bears to iodine a relation similar to that which ammonium hydroxide bears to nitrogen. Compounds of the same order are known in which sulphur plays the same part that iodine plays in the iodonium compounds, and nitrogen in the ammonium compounds.

Dibrom-benzene, $C_6H_4Br_2$, is one of the products of the direct treatment of benzene with bromine in the presence of a carrier. This being a di-substitution product of benzene, it follows, from what has been said in regard to isomerism in this series of hydrocarbons, that three isomeric varieties of the substance ought to be obtainable; and the interesting question suggests itself: which one of the three possible dibrom-ben-

zenes is formed by direct treatment of benzene with bromine? The answer to the question is equally interesting. The main product of the action is *para*-dibrom-benzene, while there is always formed in much smaller quantity some of the *ortho* product. The reason why these products are formed, and not the *meta* compound, is unknown; nor has any plausible hypothesis been suggested to account for the fact.

In studying the substitution-products of benzene, one of the first problems that presents itself is the determination of the relations which the substituting atoms or groups bear to each other. The determination is made, as has been stated, by transforming the compounds into others, the relations of whose groups are known. Thus, to illustrate, when benzene is treated under the proper conditions with bromine, two dibrom-benzenes are formed. Without investigation, we, of course, cannot tell to which series these compounds belong. But, by treating that product which is formed in larger quantity with methyl iodide and sodium, we get *para-xylene*. In other words, by replacing the two bromine atoms of the dibrom-benzene by methyl groups, we get a compound which we know belongs to the para series; and, therefore, we have determined that the bromine product is a *para compound*. In the following the chief reactions made use of for effecting the transformations of the derivatives will be discussed.

Halogen Derivatives of Toluene.

As toluene is made up of a residue of marsh gas, methyl, CH_3, and a residue of benzene, phenyl, C_6H_5, it yields two classes of substitution-products: (1) Those in which the substituting atom or group replaces one or more hydrogen atoms of the phenyl group; and (2) those in which the substitution takes place in the methyl. In general, when treated with chlorine or bromine in direct sunlight, or at the boiling temperature, toluene yields products of the second class; while,

when treated in the dark, or at low temperatures, it yields products of the first class. Thus, we have the two parallel series of chlorine derivatives: —

I.	II.
$C_6H_4Cl \cdot CH_3$.	$C_6H_5 \cdot CH_2Cl$.
$C_6H_3Cl_2 \cdot CH_3$.	$C_6H_5 \cdot CHCl_2$.
$C_6H_2Cl_3 \cdot CH_3$.	$C_6H_5 \cdot CCl_3$.

When a member of the first class is oxidized, the methyl is changed, and the rest of the compound remains unchanged, as in the case of toluene. Thus, the first substance of class I. yields the product $C_6H_4Cl \cdot CO_2H$; the second, $C_6H_3Cl_2 \cdot CO_2H$, etc. These products are *substituted benzoic acids.* On the other hand, all the members of the second class yield the same product that toluene does; viz., *benzoic acid.* Hence, by treatment with oxidizing agents, it is easy to distinguish between the members of the two classes. Further, the halogen atoms contained in the methyl react like the halogen atoms in paraffin derivatives, while those in the benzene ring do not. When, for example, the compound $C_6H_5 \cdot CHCl_2$, which is called *benzal chloride,* is superheated with water, both chlorine atoms are replaced by oxygen, the product being the aldehyde $C_6H_5 \cdot CHO$, which, as we shall see, is the familiar substance, *oil of bitter almonds.* When, however, the isomeric *di-chlor-toluene* $C_6H_3Cl_2 \cdot CH_3$ is superheated with water, no change takes place.

Regarding those simple substitution-products of toluene which contain one halogen atom in the phenyl, such as mono-brom-toluene, $C_6H_4Br \cdot CH_3$, we see that they are di-substitution products of benzene, and hence capable of existing in three isomeric varieties, ortho, meta, and para. The products formed by direct treatment of toluene with chlorine or bromine are mixtures of the para and the ortho compound.

The determination of the series to which one of these products belongs can be made by replacing the halogen by methyl, and thus getting the corresponding xylene. The main product of

the action of bromine on toluene is thus converted into para-xylene, and is therefore para-brom-toluene.

Halogen Derivatives of the Higher Members of the Benzene Series.

Concerning the halogen derivatives of xylene, it need only be said that the only one of the three xylenes from which pure products can easily be obtained is para-xylene. When this is treated with bromine it yields but one mono-brom-xylene. The significance of this fact has been discussed above. The mono-substitution products obtained from the other xylenes are mixtures which it is very difficult, and in some cases impossible, to separate into their constituents. Mesitylene and pseudocumene, though both are tri-methyl-benzenes, conduct themselves quite differently towards bromine, — the former yielding only one mono-bromine product; the latter, a mixture of several.

Nitro Compounds of Benzene and Toluene.

In speaking of nitro compounds in connection with the paraffin derivatives (see p. 100), it was stated that they are obtained much more readily from the benzene hydrocarbons than from the paraffins. Only a few nitro derivatives of the paraffins are known. As will be remembered, they cannot be prepared by treating the paraffins with nitric acid, but must be made by circuitous methods, the principal one being the treatment of the halogen derivatives with silver nitrite: —

$$C_2H_5Br + AgNO_2 = C_2H_5(NO_2) + AgBr.$$

Nitro-ethane.

The preparation of a nitro derivative of a hydrocarbon of the benzene series is a simple matter. It is only necessary to bring the hydrocarbon in contact with strong nitric acid, when reaction takes place, and one or more hydrogen atoms of the

hydrocarbon are replaced by the nitro group NO_2, as represented in the equations, —

$$C_6H_6 + HNO_3 = C_6H_5 . NO_2 + H_2O;$$

$$C_6H_5 . NO_2 + HNO_3 = C_6H_4(NO_2)_2 + H_2O;$$

$$C_6H_5 . CH_3 + HNO_3 = C_6H_4 < \begin{matrix} NO_2 \\ CH_3 \end{matrix} + H_2O;$$

$$C_6H_4 < \begin{matrix} NO_2 \\ CH_3 \end{matrix} + HNO_3 = C_6H_3 < \begin{matrix} (NO_2)_2 \\ CH_3 \end{matrix} + H_2O.$$

The nitro compounds thus obtained are not acids, nor are they esters of nitrous acid. If they were esters of nitrous acid they would be saponified by caustic alkalies, yielding a nitrite and hydroxyl derivatives similar to the alcohols. They do not act in this way. When treated with nascent hydrogen they are reduced to amino compounds or substituted ammonias. Thus, nitrobenzene, $C_6H_5 . NO_2$, gives aniline or amino-benzene, $C_6H_5 . NH_2$, which is a substituted ammonia similar to methylamine and ethylamine. As in these the radical is in combination with nitrogen, it is probable that the radical is in combination with nitrogen in the nitro compounds also, as shown in the formula, $C_6H_5 . NO_2$. Everything known about these nitro compounds is in harmony with this view. The formation of a nitro compound by the action of nitric acid on a hydrocarbon is represented thus: —

$$C_6H_5H + HO . NO_2 = C_6H_5 . NO_2 + H_2O.$$

Mono-nitro-benzene, $C_6H_5 . NO_2$. — This substance is made by treating benzene with concentrated nitric acid, or with a mixture of ordinary concentrated nitric and sulphuric acids. In the latter case, the sulphuric acid facilitates the reaction, probably by preventing the dilution of the nitric acid by the water necessarily formed.

Experiment 58. Make a mixture of 150^{cc} ordinary concentrated sulphuric acid, and 75^{cc} ordinary concentrated nitric acid. Let it cool

to the ordinary temperature. Put the vessel containing it in water, and add about 15cc to 20cc benzene, a few drops at a time, waiting each time until the reaction is complete. Shake well until the benzene is dissolved; then pour slowly into about a litre of cold water. A yellow oil will sink to the bottom. This is nitro-benzene. Pour off the acid and water; wash two or three times with water; separate the water by means of a pipette, and dry by adding a little granulated calcium chloride. After standing for some time, pour off from the calcium chloride, and distil from a proper sized distilling-bulb, noting the boiling temperature.

Nitro-benzene is a liquid that boils at 205°, solidifies at 3°, and has the specific gravity 1.2. Its odor is like that of the oil of bitter almonds, and it is hence used in many cases instead of the latter. It is known as the *essence of mirbane.* It is manufactured on the large scale, and used principally in the preparation of aniline. Its vapor is poisonous.

Dinitro-benzene, $C_6H_4(NO_2)_2$. — This is a product of the further action of nitric acid on benzene, or on nitro-benzene.

Experiment 59. Make a mixture of 50cc concentrated sulphuric acid, and 50cc *fuming* nitric acid. Without cooling add *very slowly* about 10cc benzene from a pipette with a fine opening. After the action is over, boil the mixture for a short time; then pour into about half a litre of water. Filter off the solid substance thus precipitated, press it between layers of filter-paper, and crystallize from alcohol.

Dinitro-benzene crystallizes in long, fine needles, or thin, rhombic plates. Melting-point, 91°.

By means of two reactions, which will be described under the head of Diazo Compounds, it is a simple matter to replace the two nitro groups by bromine, thus converting dinitro-benzene into dibrom-benzene. When the latter is converted into xylene, the product is meta-xylene. Hence, ordinary dinitro-benzene is a meta compound.

Nitro-toluenes, $C_6H_4(NO_2).CH_3$. — When toluene is treated with strong nitric acid, substitution always takes place in the phenyl. The chief mono-nitro-toluene is a para compound;

while, at the same time, a little of the isomeric ortho compound is obtained.

NOTE FOR STUDENT. — What mono-bromine products are formed by direct treatment of toluene with bromine? Given a mono-nitro-toluene, how is it possible to determine whether it belongs to the ortho, the meta, or the para series?

By treatment with nascent hydrogen, the nitro-toluenes are converted into the corresponding amino compounds, called *Toluidines* (which see).

AMINO COMPOUNDS OF BENZENE, ETC.

The amino derivatives of the paraffins are made, for the most part, by treating the halogen derivatives with ammonia: —

$$C_2H_5Br + NH_3 = C_2H_5 . NH_2 + HBr.$$

In speaking of these derivatives, however, attention was called to the fact that they can also be made by treating nitro compounds with nascent hydrogen. The latter method is one of great importance in the benzene series. It is used exclusively in the preparation of the amino derivatives of the benzene hydrocarbons. Several of these derivatives are well known, the simplest and best known being *amino-benzene* or *aniline*.

Aniline, $C_6H_7N (= C_6H_5 . NH_2)$. — Aniline was first obtained from indigo by distillation. *Anil* is the Portuguese and French name of the indigo plant, and it is from this that the name aniline is derived. Aniline is found in coal tar and in bone oil, a product of the distillation of bones. It is prepared by reducing nitro-benzene with nascent hydrogen. On the large scale the hydrogen is obtained from hydrochloric acid and iron. For laboratory purposes tin and hydrochloric acid are perhaps best. Other reducing agents, such as an ammoniacal solution of ammonium sulphide, hydriodic acid, etc., also effect the change, which is represented by the following equation: —

$$C_6H_5 . NO_2 + 6 H = C_6H_5 . NH_2 + 2 H_2O.$$

Experiment 60. Arrange a litre flask with a stopper and a straight glass tube from two to three feet long. Put in the flask 85g granulated tin and about 400g ordinary concentrated hydrochloric acid. Now add *slowly* 50g nitro-benzene. After the action is over, add enough water to dissolve the contents of the flask, then add sodium hydroxide until the precipitate first formed is nearly all dissolved. Distil, when aniline and water will pass over. Separate as in the case of brom-ethane (see p. 30).

Aniline is a colorless liquid which soon becomes colored in the air. It boils at 182.5°. It solidifies at a low temperature and melts at $-8°$; it is easily soluble in alcohol, but slightly soluble in water. The solution in water has only a slight alkaline reaction.

Experiment 61. To an aqueous solution of a little of the aniline obtained in Exp. 60, in a test-tube, add a filtered solution of bleaching powder (calcium hypochlorite). A beautiful purple color is produced.

To a solution of aniline in concentrated sulphuric acid add a few drops of an aqueous solution of potassium bichromate. A blue color is produced.

The reaction with bleaching powder is due to an impurity that is always found in aniline unless it has been specially purified. Pure aniline does not give this reaction.

Aniline bears to benzene the same relation that ethyl-amine or amino-ethane bears to ethane. It is a substituted ammonia, and, like other bodies of the same class, it unites directly with acids, forming salts. Thus, with hydrochloric, nitric, and sulphuric acids the action takes place as represented below: —

$$C_6H_5 . NH_2 + HCl = (C_6H_5 . NH_3) Cl;$$
$$C_6H_5 . NH_2 + HNO_3 = (C_6H_5 . NH_3) NO_3;$$
$$C_6H_5 . NH_2 + H_2SO_4 = C_6H_5 . NH_3HSO_4.$$

The hydrochloride is known in the trade as *aniline salt*.

The decomposition of aniline hydrochloride by means of a caustic alkali takes place as represented in the following equation: —

$$C_6H_5 . NH_3Cl + KOH = C_6H_5 . NH_2 + H_2O + KCl.$$

Derivatives of Aniline. — Aniline is much more sensitive to the action of reagents than benzene or its halogen or nitro derivatives. Substitution takes place easily, but there is danger that the aniline will be decomposed by the substituting agent. Among the substitution-products that find extensive application is one of the sulphonic acids.

Dimethyl-aniline, $C_6H_5 . N(CH_3)_2$. — When aniline is treated with methyl bromide and similar halogen derivatives of the paraffins, residues of the paraffins are introduced into the aniline in place of the ammonia hydrogen atoms: —

$$C_6H_5 . NH_2 + CH_3Br = [C_6H_5 . NHCH_3] . HBr;$$

$$C_6H_5 . NH_2 + 2\,CH_3Br = [C_6H_5 . N(CH_3)_2] . HBr + HBr.$$

Of the compounds obtainable by this method, dimethyl-aniline is the most important from the technical point of view. It is prepared by a modification of the above method — by heating aniline with hydrochloric or sulphuric acid and methyl alcohol in a closed vessel: —

$$C_6H_5 . NH_2 . HCl + CH_3OH = C_6H_5 . NH_2 + CH_3Cl + H_2O;$$

$$C_6H_5 . NH_2 + CH_3Cl = C_6H_5 . NH(CH_3) . HCl;$$

$$C_6H_5 . NH(CH_3) . HCl + CH_3OH = C_6H_5 . N(CH_3)_2 . HCl + H_2O.$$

It is a liquid that boils at 193°, and solidifies at 0.5°.

Diphenylamine $(C_6H_5)_2NH$. — This is another example of the possibilities presented by aniline. As will be seen, diphenylamine is formed from aniline by the introduction of a phenyl group, C_6H_5, for one of the ammonia hydrogen atoms. It is prepared on the large scale, and finds extensive use in the manufacture of dyes. The reaction made use of consists in heating aniline with aniline hydrochloride at 200°: —

$$C_6H_5 . NH_2 + C_6H_5 . NH_2 . HCl = C_6H_5 . NH . C_6H_5 + NH_4Cl.$$

It is a solid that crystallizes in white laminæ from ligroin.

It melts at 54° and boils at 302°. It forms salts with strong acids, but these are decomposed by water.

Acetanilide, $C_6H_5 . NH . COCH_3$. — Aniline reacts with acid chlorides as ammonia does. While ammonia forms amides, aniline forms *anilides*. Thus, with acetyl chloride, ammonia gives acetamide, and aniline gives acetanilide: —

$$CH_3 . COCl + NH_3 = CH_3 . CONH_2 + HCl;$$

$$CH_3 . COCl + NH_2 . C_6H_5 = CH_3 . CO . NH . C_6H_5 + HCl.$$

Acetanilide is more easily prepared by heating aniline and glacial acetic acid together: —

$$CH_3 . COOH + NH_2 . C_6H_5 = CH_3 . CO . NH . C_6H_5 + H_2O.$$

Acetanilide crystallizes from water in large, colorless plates. It melts at 115° and boils at 304°. It is used in medicine under the name *antifebrine*.

Toluidines, amino-toluenes, $C_6H_4 < \begin{matrix} NH_2 \\ CH_3 \end{matrix}$. — The toluidines, of which there are three corresponding to the three nitro-toluenes, are made from the latter in the same way that aniline is made from nitro-benzene. As *para-nitro-toluene* is the best known of the three nitro-toluenes, so *para-toluidine* is the best known of the three toluidines.

The properties of the toluidines are much like those of aniline.

Treated with various oxidizing agents, a mixture of aniline and the toluidines is converted into a compound known as *rosaniline*. This is the mother substance of the large group of compounds known as the *aniline dyes*. Rosaniline and its derivatives, the aniline dyes, will be treated under *Tri-phenyl-methane* (which see).

By nitrous acid the toluidines are transformed in the same way that aniline is (see Diazo Compounds).

The **xylidines** bear to the three xylenes the same relation that aniline bears to benzene. It is not a simple matter to get any one of them in pure condition.

Diazo Compounds of Benzene, etc.

The usual action of nitrous acid on amino compounds is represented by the equation, —

$$R.NH_2 + HNO_2 = R.OH + H_2O + N_2.$$

When an amino derivative of a hydrocarbon of the benzene series is treated with nitrous acid at low temperatures, a product is obtained which contains two nitrogen atoms, and which is, therefore, called a *diazo compound.* Thus, in the case of aniline sulphate, the action is represented by the equation, —

$$\underset{\text{Aniline sulphate.}}{C_6H_5NH_2.H_2SO_4} + HNO_2 = \underset{\text{Benzene-diazonium sulphate.}}{C_6H_5N_2.HSO_4} + 2\,H_2O.$$

So, also, with the nitrate we have, —

$$\underset{\text{Aniline nitrate.}}{C_6H_5NH_2.HNO_3} + HNO_2 = \underset{\text{Benzene-diazonium nitrate.}}{C_6H_5N_2.NO_3} + 2\,H_2O.$$

The salts thus formed are called *diazonium salts* for reasons which will presently be given. From them the benzene-diazonium hydroxide itself cannot be set free.

Experiment 62. Arrange an apparatus as shown in Fig. 14. In flask *A* put arsenic trioxide (about 50g), and through the funnel-tube pour 40cc to 50cc ordinary nitric acid (sp. gr. 1.35). *B* is an empty cylinder surrounded by water. *C* is a test-tube of about 50cc capacity. In it should be brought 10g aniline nitrate, and 12cc ice-cold water. This is placed in *ice water.* Pass a current of the oxides of nitrogen until the material in the tube dissolves. Add to the solution about an equal volume of alcohol previously cooled to 0°, and then a little cold ether. If the operation has been successful, a copious precipitate of crystals of *benzene-diazonium nitrate* will appear. Filter off with the aid of a suction-pump, and, *without delay*, proceed to study the properties of the compound.

(*a*) Dissolve a little in water of the ordinary temperature, and allow the solution to stand. Decomposition, indicated by change of color, will take place.

(*b*) Boil a little with water in a test-tube, and notice the odor of phenol or carbolic acid.

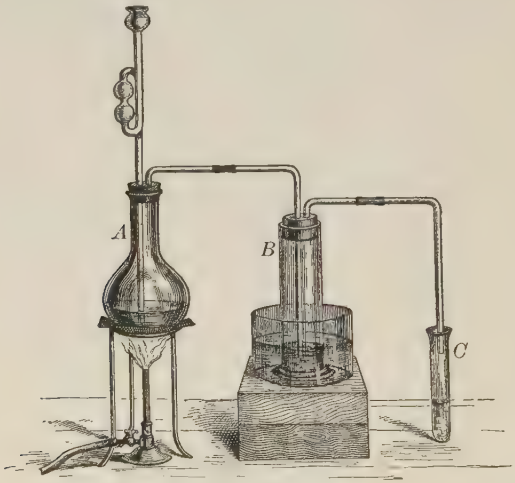


Fig. 14.

(*c*) Boil a few grams with alcohol in a test-tube, and notice the ease with which the decomposition takes place. The chief product is ethyl-phenyl ether or phenetol, $C_6H_5 . O . C_2H_5$.

(*d*) Boil some with concentrated hydrochloric acid. Chlor-benzene is formed, which sinks to the bottom when water is added.

In all these experiments a gas is evolved which can be shown to be nitrogen. Collect some, and show that it does not support combustion.

(*e*) Place a very little of the compound, dried by pressing in filter-paper, on an anvil, and strike it sharply with a hammer. It explodes.

The above experiments serve to indicate the instability of benzene-diazonium nitrate. This same instability is characteristic of all diazonium salts, and it is the ease with which they

undergo a variety of changes that makes them so valuable. The principal changes are: —

1. That illustrated in Exp. 62 (*b*), which is brought about by boiling with water. The action is represented thus: —

$$C_6H_5N_2 . NO_3 + H_2O = \underset{\text{Phenol.}}{C_6H_5 . OH} + N_2 + HNO_3.$$

2. That illustrated in Exp. 62 (*c*), which is effected by boiling with alcohol: —

$$C_6H_5N_2 . NO_3 + C_2H_5 . OH = \underset{\text{Phenetol.}}{C_6H_5 . O . C_2H_5} + N_2 + HNO_3.$$

In some cases alcohol reacts in another way, thus: —

$$RN_2Cl + C_2H_5OH = RH + N_2 + C_2H_4O + HCl.$$

The result of this is the substitution of hydrogen for the diazo group. Sometimes both reactions take place with alcohol.

3. That effected by hydrochloric acid as illustrated in Exp. 62 (*d*): —

$$C_6H_5N_2 . NO_3 + HCl = \underset{\text{Mono-chlor-benzene.}}{C_6H_5Cl} + N_2 + HNO_3.$$

This reaction is much facilitated by cuprous chloride (Sandmeyer's reaction).

Changes similar to the last are effected by hydrobromic and hydriodic acids, the chief products being brom-benzene and iodo-benzene respectively. Here also the corresponding cuprous salts are of great assistance.

From the above it follows that, if we have a compound containing a nitro group, we can, by making the diazonium salt, transform it (1) into the corresponding hydroxyl derivative; (2) into the corresponding chlorine, bromine, or iodine derivative; or, (3) we can make ethers containing such groups as C_2H_5O, CH_3O, etc. These reactions involving the use of the diazonium salts have been used very extensively in the investigation of the substitution-products of the benzene series.

Note for Student. — How can the relation of the groups in dinitrobenzene be determined by using the diazonium reactions?

Constitution of the Salts of Diazo Compounds. — The salts formed by the action of nitrous acid on aniline salts are salts of a strong base which are to be compared with the alkali salts. It has been shown by determinations of the freezing point and of the electrical conductivity of the solutions of these salts in water that they are broken down into ions in the same way as salts of strong bases. This suggests that they are analogous to ammonium salts, and the view that is most in accordance with all the facts is that represented by such formulas as the following: —

$$\begin{array}{ccc} C_6H_5.N-Cl & C_6H_5.N-NO_3 & C_6H_5-N-HSO_4 \\ \quad\;\; ||| & \quad\;\; ||| & \quad\;\; ||| \\ \quad\;\; N & \quad\;\; N & \quad\;\; N \end{array}$$

As the salts are analogous to ammonium salts, they are called *diazonium salts.* According to this view they are to be regarded as aniline salts into which a nitrogen atom has been introduced in place of three hydrogen atoms: —

$$\begin{array}{ccc} C_6H_5-N-Cl & \longrightarrow & C_6H_5-N-Cl; \\ \quad\;\; ||| & & \quad\;\; ||| \\ \quad\;\; H_3 & & \quad\;\; N \end{array}$$

$$\begin{array}{ccc} C_6H_5-N-NO_3 & \longrightarrow & C_6H_5-N-NO_3. \\ \quad\;\; ||| & & \quad\;\; ||| \\ \quad\;\; H_3 & & \quad\;\; N \end{array}$$

Metallic Derivatives of Diazo-benzene and of Isodiazo-benzene. — When a diazonium salt is treated in the cold with caustic potash a potassium salt of the formula $C_6H_5.N_2.OK$ is formed. When this is treated with ethyl iodide it gives an ether of diazo-benzene, $C_6H_5.N_2.OC_2H_5$. The fact that the ethyl in this compound is in combination with oxygen is shown by the character of the products formed when it is decomposed. It does not yield ethylamine as it would if the ethyl were in combination with nitrogen. When the above-mentioned potassium salt is treated with phenols (which see), it reacts with them at once, forming azo compounds (which see).

When the ordinary potassium salt of diazo-benzene is heated with concentrated caustic potash at 130°, it is converted into *iso-diazo-benzene potassium* by molecular rearrangement. This does not give azo compounds with phenols. With ethyl iodide it gives a compound in which the ethyl is in combination with nitrogen. It is a nitroso compound of the formula $C_6H_5 . N < \begin{matrix} C_2H_5 \\ NO \end{matrix}$.

The facts above stated suggest that the ordinary or normal diazo-benzene potassium has the structure represented by the formula $C_6H_5 - N_2 - OK$, and that iso-diazo-benzene potassium has the formula $C_6H_5 - NK . NO$, and that they correspond to the two diazo-benzenes: —

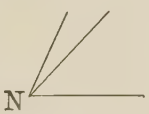
$C_6H_5 . N_2 . OH$	$C_6H_5 . NH . NO$
Diazo-benzene.	Iso-diazo-benzene.

These formulas do not, however, appear probable in view of other facts.

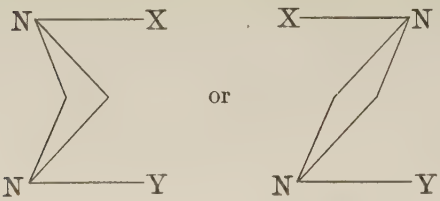
It has been suggested that the two potassium salts and other similar salts are stereoisomeric, as represented in the formulas: —

$C_6H_5 - N$ ‖ $KO . N$	$C_6H_5 - N$ ‖ $N . OK$
Diazo-benzene potassium.	Iso-diazo-benzene potassium.

By way of explanation of these formulas, it should be said that they involve the conception that the nitrogen atom exerts its affinities in the direction of three edges of a tetrahedron, thus: —



When combined with another nitrogen atom by double union the figures representing this condition would be: —



There are two ways in which the groups or atoms X and Y can be arranged in space, or there should be two isomeric forms of compounds containing a group of two nitrogen atoms of the form $-N=N-$.

Diazo-amino Compounds. — When a diazonium salt reacts with an amino compound a *diazo-amino compound* is formed, as, for example, when benzene-diazonium chloride acts upon aniline: —

$$C_6H_5 . N_2Cl + NH_2 . C_6H_5 = C_6H_5N_2 . NH . C_6H_5 + HCl.$$

As will be seen, the residue of the diazonium salt takes the place of one of the hydrogen atoms of the amino group. *Diazo-amino-benzene* forms golden yellow laminæ or prisms. It is insoluble in water, but readily in hot alcohol. When heated with aniline it is transformed into *amino-azo-benzene:* —

$$C_6H_5 . N_2 . NH . C_6H_5 \longrightarrow C_6H_5 . N_2 . C_6H_4 . NH_2.$$

Other diazo-amino compounds act in the same way. The product formed in the above case is an amino derivative of a compound of the formula $C_6H_5 . N_2 . C_6H_5$, known as *azo-benzene.*

Azobenzene, $C_6H_5 . N_2 . C_6H_5$, is formed by partial reduction of nitro-benzene in alkaline solution, as by treating with an alcoholic solution of caustic potash. It crystallizes from alcohol in orange-red, rhombic crystals. Reducing agents convert it into *hydrazo-benzene*, $C_6H_5 . NH . NHC_6H_5$. *Azo compounds* are, in general, highly colored, and many of them are

used as dyes. Those that are useful in this way are derivatives of the simple azo compounds, especially those containing the sulphonic acid group, SO_3H. Some of them will be mentioned in other connections.

Hydrazo-benzene, $C_6H_5 . NH . NH . C_6H_5$, is formed by reduction of azo-benzene. It is made by reduction of nitrobenzene by means of zinc dust in alkaline solution, without isolating the azo-benzene which is formed as an intermediate product. It forms colorless laminæ, is scarcely soluble in water, but easily in alcohol and ether. Under the influence of mineral acids, hydrazo-benzene is transformed into the isomeric *benzidine,*

$$\begin{array}{l} C_6H_4 . NH_2 \\ | \\ C_6H_4 . NH_2 : \end{array}$$

$$\begin{array}{ccc} C_6H_5 . NH & & C_6H_4 . NH_2 \\ | & \longrightarrow & | \\ C_6H_5 . NH & & C_6H_4 . NH_2 . \\ \text{Hydrazo-benzene.} & & \text{Benzidine.} \end{array}$$

Reduction-products of Nitro-benzene. — The final reduction-product of nitro-benzene is amino-benzene or aniline, but by regulating the conditions, a number of intermediate products can be obtained. In addition to those already mentioned there are two others, *azoxy-benzene,* $C_6H_5 . N_2O . C_6H_5$, and *phenyl-hydroxylamine,* $C_6H_5 . NH (OH)$.

The following table will serve to emphasize the relations between most of these products: —

$$\begin{array}{ccccc} C_6H_5 . NO_2 & \begin{array}{l} C_6H_5 . N \\ \quad\quad | \\ C_6H_5 . N \end{array} \!\!> O & \begin{array}{c} C_6H_5 . N \\ \quad\quad \| \\ C_6H_5 . N \end{array} & \begin{array}{c} C_6H_5 . NH \\ \quad\quad | \\ C_6H_5 . NH \end{array} & C_6H_5 . NH_2 \\ \text{Nitro-benzene.} & \text{Azoxy-benzene.} & \text{Azo-benzene.} & \text{Hydrazo-benzene.} & \text{Aniline.} \end{array}$$

These compounds are representatives of classes of similar structure and properties.

Hydrazines.

Hydrazo-benzene is a derivative of hydrazine, $NH_2 . NH_2$, and may be called symmetrical diphenylhydrazine in view of the fact that the two phenyl groups contained in it are symmetrically distributed, as shown by the formula, $C_6H_5 . NH . NH . C_6H_5$. The simplest representative of the class of aromatic hydrazines is phenylhydrazine, $C_6H_5 . NH . NH_2$, a compound which, as has been seen, has played an important part in the investigation of the sugars.

Phenylhydrazine, $C_6H_5 . NH . NH_2$. — This is formed by the reduction of diazonium salts: —

$$\underset{\text{Benzene diazonium chloride.}}{C_6H_5 . N_2Cl} + 4\,H = \underset{\text{Phenylhydrazine hydrochloride.}}{C_6H_5 . NH . NH_2 . HCl}.$$

It forms crystals that melt at 23°. It boils at 242°. It finds extensive application in connection with the manufacture of *antipyrine* (which see).

Phenylhydrazine is a monacid base, and forms well-characterized salts. It reacts with aldehydes and with ketones, forming hydrazones (see page 190).

Sulphonic Acids of Benzene, etc.

The methods of preparation of the sulphonic acids, and the relations of these acids to the hydrocarbons, were pretty fully discussed in connection with the paraffins. Three general methods for their preparation were given. These are: —

1. Oxidation of the mercaptans; thus, ethyl-sulphonic acid is formed by oxidation of ethyl-mercaptan: —

$$C_2H_5 . SH + 3\,O = C_2H_5 . SO_3H.$$

2. Treatment of a halogen substitution-product with a sulphite, — $C_2H_5Br + Na_2SO_3 = C_2H_5 . SO_3Na + NaBr$.

3. Treatment of a hydrocarbon with sulphuric acid. This

method is not applicable to the paraffins, but is the one used almost exclusively in the case of the benzene hydrocarbons. This reaction is characteristic of the aromatic compounds. Benzene-sulphonic acid is formed thus: —

$$C_6H_6 + H_2SO_4 = C_6H_5.SO_3H + H_2O.$$

Toluene-sulphonic acid is formed thus: —

$$C_6H_5.CH_3 + H_2SO_4 = C_6H_4 < \begin{matrix} CH_3 \\ SO_3H \end{matrix} + H_2O.$$

The reasons for regarding the sulphonic acids as sulphuric acid in which hydroxyl is replaced by radicals, were given on p. 76; and the student is advised carefully to re-read what is there said.

Benzene-sulphonic acid, $C_6H_6SO_3\left(=\begin{matrix} C_6H_5 \\ HO \end{matrix}\right\}SO_2\right)$. — This acid is made by treating benzene with sulphuric acid. Similarly, and more easily, *toluene-sulphonic acid*, $C_7H_7.SO_3H$, is made from toluene.

Experiment 63. In a flask bring together about 50cc toluene and 100cc concentrated sulphuric acid (ordinary). Heat on a water-bath and shake until most of the toluene is dissolved. Pour the contents of the flask into a large evaporating dish of at least 8l to 10l capacity, containing 4l to 5l water. Heat gently, and add gradually, stirring meanwhile, *finely-powdered* chalk, until the solution has become neutral. Pass through a muslin filter attached to a wooden frame, and wash thoroughly with hot water. Afterwards refilter the filtrate through a paper filter. Evaporate to quite a small volume (say 500cc to 700cc), and filter from gypsum. In solution there is now the calcium salt of the sulphonic acid. Add just enough of a solution of sodium carbonate to precipitate exactly the calcium; filter off from the calcium carbonate, and evaporate to dryness, finally, on the water-bath. To prevent caking it is necessary to stir the thick, syrupy mass. When it is nearly dry, it is best to powder it, and complete the drying at 100° to 120° in an air-bath. The sodium salt can be used for a number of experiments.

Experiment 64. In a dry evaporating dish mix thoroughly 20g of sodium toluene-sulphonate with 25g of phosphorus penta-chloride, by means of a dry pestle. The mass becomes semi-liquid and hot, and hydrochloric acid is given off, in consequence of the action of the moisture of the air on the chlorides of phosphorus. Hence, the experiment should be performed under a hood or out of doors. The reaction which takes place is represented by the equation, —

$$C_7H_7.SO_2ONa + PCl_5 = C_7H_7.SO_2Cl + POCl_3 + NaCl.$$

After the action is over, and the mass cooled down to the ordinary temperature, add about a litre of cold water. Everything will dissolve except the sulphon-chloride, $C_7H_7.SO_2Cl$, which will remain as a heavy oil at the bottom of the vessel. Pour off the water, add about 500cc of strong ammonia, and let stand. The chloride will thus be converted into the corresponding sulphon-amide, thus: —

$$C_7H_7.SO_2Cl + 2\,NH_3 = C_7H_7.SO_2NH_2 + NH_4Cl.$$

After cooling, filter off the sulphon-amide; wash well with cold water, and crystallize from water.

Note for Student. — Refer back to what was said regarding the acid chlorides and acid amides, paying particular attention to the general methods of preparation and their decompositions.

Experiment 65. Mix 20g potassium cyanide with an equal weight of dry potassium toluene-sulphonate, and distil from a small retort. The distillate is impure tolyl cyanide, $C_7H_7.CN$: —

$$\left.\begin{matrix} C_7H_7 \\ KO \end{matrix}\right\rangle SO_2 + KCN = C_7H_7.CN + K_2SO_3.$$

Put the tolyl cyanide in a flask of 300cc to 400cc capacity, and add a mixture of 50cc water and 150cc ordinary concentrated sulphuric acid. Heat on a sand-bath until the toluic acid begins to appear in the form of fine, white needles in the neck of the flask. On cooling, the acid will crystallize out. Pour off the liquid, and wash with cold water. Now crystallize the acid once or twice from water. When pure, para-toluic acid melts at 177°. The reaction is represented by the following equation: —

$$C_7H_7.CN + 2\,H_2O = C_7H_7.CO_2H + NH_3.$$

Benzene-sulphonic acid itself is a very easily soluble sub-

stance. It is a strong acid, and yields a series of salts and other derivatives.

When fused with potassium hydroxide, benzene-sulphonic acid is converted into phenol (Exp. 66, p. 298): —

$$C_6H_5 . SO_3K + KOH = C_6H_5 . OH + K_2SO_3.$$

By further treatment of benzene with fuming sulphuric acid a benzene-disulphonic acid is formed. This is capable of the same transformations as the mono-sulphonic acid.

Note for Student. — By what reaction could benzene-disulphonic acid be transformed into the corresponding dicarbonic acid, $C_6H_4(CO_2H)_2$? Suppose the product obtained were meta-phthalic acid, what conclusion could be drawn with reference to the relation of the two sulpho groups, SO_3H, in the disulphonic acid?

Sulphanilic acid, $C_6H_4 < \begin{matrix} NH_2 \\ SO_3H \end{matrix}$. — When aniline is treated with concentrated sulphuric acid, aniline sulphate, $C_6H_5NH_3 . HSO_4$, is first formed. Further action converts this into the para-sulphonic acid, $C_6H_4 < \begin{matrix} NH_2 \\ SO_3H(p) \end{matrix}$:

$$C_6H_5 . NH_3 . HSO_4 = C_6H_4 < \begin{matrix} NH_2 \\ SO_3H \end{matrix} + H_2O.$$

Sulphanilic acid is difficultly soluble in cold water, more easily in hot water. It crystallizes from a solution in water in rhombic plates.

Like taurine, it is probably an inner ammonium salt, and should, therefore, be represented thus, $C_6H_4 < \begin{matrix} NH_3 \\ SO_3 \end{matrix} >$. It is, however, a strong acid, while taurine is neutral. This is accounted for by the fact that aniline is a much weaker base than ethylamine. In taurine the basic portion has the power to neutralize the acid portion, while in sulphanilic acid this is not the case. Sulphanilic acid finds extensive application in the manufacture of dyes.

Helianthin, methyl orange, tropæolin D, is an example of the azo dyes already referred to. It is formed by the action of diazobenzene-sulphonic acid on dimethyl-aniline. The diazobenzene-sulphonic acid is made from sulphanilic acid: —

$$(1)\quad \underset{\text{Sulphanilic acid.}}{C_6H_4{<}\begin{matrix}NH_3\\SO_3\end{matrix}{>}} \longrightarrow \underset{\text{Diazobenzene-sulphonic acid.}}{C_6H_4{<}\begin{matrix}N_2\\SO_3\end{matrix}{>}}$$

$$(2)\quad \underset{\text{Diazobenzene-sulphonic acid.}}{C_6H_4{<}\begin{matrix}N_2\\SO_3\end{matrix}{>}} + \underset{\text{Dimethyl-aniline.}}{C_6H_5.N(CH_2)_2} = \underset{\text{Dimethyl-aniline-azo-benzene-sulphonic acid.}}{\begin{matrix}C_6H_4.N_2.C_6H_4.N(CH_3)_2\\|\\SO_3H\end{matrix}}$$

The product here represented is methyl-orange. It is not used as a dye, though it has marked coloring power.

Diphenylamine orange, tropæolin OO, is another example of the azo dyes. It is made by the action of diazotized sulphanilic acid on diphenyl-amine: —

$$C_6H_4{<}\begin{matrix}N_2\\SO_3\end{matrix}{>} + \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}NH = \begin{matrix}C_6H_4.N_2.C_6H_4.NH.C_6H_5.\\|\\SO_3H\end{matrix}$$

The sulphonic acid thus formed is the acid of which diphenylamine orange is the sodium salt.

Phenols, or Hydroxyl Derivatives of Benzene, etc.

The hydroxyl derivatives of the paraffins are called *alcohols.* As will be remembered, they are of three kinds, each of which is characterized by certain properties. These are: —

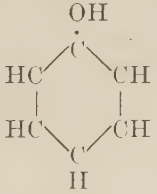
1. *Primary alcohols,* of which ordinary ethyl alcohol is the commonest example, and which, when oxidized, yield aldehydes and then acids containing the same number of carbon atoms.

2. *Secondary alcohols,* which by oxidation yield acetones and then acids containing a smaller number of carbon atoms.

3. *Tertiary alcohols*, which by oxidation yield neither aldehydes nor acetones, but break down at once, yielding acids with a smaller number of carbon atoms.

The primary alcohols were shown to correspond to the formula $C\begin{cases} R \\ H \\ H \\ HO \end{cases}$; the secondary to $C\begin{cases} R \\ R \\ H \\ HO \end{cases}$; and the tertiary to $C\begin{cases} R \\ R \\ R \\ HO \end{cases}$; or, in other words, the primary alcohols contain the group $CH_2.OH$; the secondary, the group $CH.OH$; and the tertiary, the group $C.OH$.

Now, the simplest hydroxyl derivative of the members of the benzene series is phenol, $C_6H_5.OH$, or benzene in which one hydrogen is replaced by hydroxyl. Representing this compound in terms of the accepted benzene hypothesis, we have the formula



According to this, phenol appears to be allied to the tertiary alcohols, as it contains the group $C.OH$, and not CH_2OH nor $CH.OH$. We shall see that, in fact, phenol conducts itself towards oxidizing agents like the tertiary alcohols. It yields neither aldehydes nor ketones.

All compounds which contain hydroxyl in the place of the benzene-hydrogen atoms of benzene and its homologues are called *phenols*. As in the case of alcohols, there are phenols containing one hydroxyl, or *mon-acid phenols*; those containing

two hydroxyls, or *di-acid phenols;* those containing three hydroxyls, or *tri-acid phenols*, etc. Some of these are familiar substances.

Mon-acid Phenols.

Phenol, carbolic acid, $C_6H_6O(C_6H_5OH)$. — Phenol is found in small quantities in the urine. It is formed by the distillation of wood, coal, and bones. Hence, it is a constituent of coal tar, and from this it is prepared. For this purpose the *heavy oil* (see p. 250) is treated with an alkali which dissolves the phenol. From the solution it is precipitated by hydrochloric acid. It is purified by distillation.

Phenol can also be made by converting nitro-benzene into aniline; then into diazo-benzene, and boiling this with water (see Exp. 62 (*b*)); and by melting benzene-sulphonic acid with potassium hydroxide.

Experiment 66. In a silver (or iron) crucible, or evaporating dish, melt 40^g to 50^g potassium hydroxide, after adding a few cubic centimetres of water. Now add gradually 10^g finely-powdered sodium toluene-sulphonate, obtained in Exp. 63, stirring constantly with a silver (or iron) spatula. Do not heat to a very high temperature. After the mass has been kept in a state of fusion for one-quarter to one-half an hour, let it cool. Dissolve in 200^{cc} to 250^{cc} water, and acidify with hydrochloric acid. Notice the odor of the gases given off. What gas do you detect? When the liquid has cooled down, extract with ether in a glass-stoppered cylinder. From the ether extract distil the ether on a water-bath. The residue is impure cresol (p. 303). Phenol can be detected by the following reactions, for which a solution in water should be prepared: —

(*a*) A few drops of ferric chloride solution gives a beautiful blue color.

(*b*) Add one-fourth volume of ammonia, and then a few drops of a dilute solution of bleaching powder. A blue color is produced.

(*c*) Bromine water gives a yellowish-white precipitate of tri-bromphenol.

The reaction which takes place in melting potassium hydroxide and potassium benzene-sulphonate together is represented by the equation, —

$$C_6H_5 . SO_3K + KOH = C_6H_5 . OH + K_2SO_3.$$

It effects the replacement of the sulpho group, SO_3H, by hydroxyl. Phenol is made by this method on the large scale.

Phenol, when pure, crystallizes in beautiful colorless rhombic needles. The presence of a little water prevents it from solidifying. It has a peculiar, penetrating odor; boils at 180°; is difficultly soluble in water (1 part in 15 parts water at ordinary temperature); mixes with alcohol and ether in all proportions; and is poisonous. It is a valuable antiseptic, and finds extensive application as a disinfectant and in the manufacture of picric acid.

A dilute solution of phenol is colored violet by a little ferric chloride.

Bromine water gives a precipitate of tri-brom-phenol when added to a water solution of phenol.

Phenol is not soluble in alkaline carbonates. Its acid properties are not strong enough to enable it to decompose these carbonates. On the other hand, it forms salts with the alkalies and with several strong bases. Among these may be mentioned the following: —

Potassium phenolate, $C_6H_5 . OK$, made by dissolving potassium in phenol, and by treating phenol with a solution of caustic potash.

Barium phenolate, $(C_6H_5O)_2Ba + 2\,H_2O$, made by dissolving phenol in baryta water.

Lead oxide phenol, $C_6H_6O . PbO$, made by dissolving lead oxide in phenol.

Phenol also forms ethers, of which the methyl, ethyl, and diphenyl ethers may serve as examples: —

Methyl-phenyl ether, $C_7H_8O\left(\begin{matrix}C_6H_5\\CH_3\end{matrix}>O\right)$. — This substance, also called *anisol*, is obtained from anisic acid (methoxy-benzoic acid) by boiling with baryta water. It is

made also by treating potassium phenolate, C_6H_5OK, with methyl iodide: —

$$C_6H_5OK + CH_3I = \begin{matrix} C_6H_5 \\ CH_3 \end{matrix} > O + KI.$$

It is a liquid of a pleasant odor.

NOTE FOR STUDENT. — Compare this substance with *ordinary ether*. What method analogous to that above mentioned can be used in the preparation of ordinary ether?

Ethyl-phenyl ether, $C_8H_{10}O \left(\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix} > O\right)$, is called *phenetol.*

Diphenyl ether, $C_{12}H_{10}O \left(\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > O\right)$. — This bears to phenol the same relation that ordinary ether bears to alcohol.

With acids, phenol, like the alcohols, yields ethereal salts in which the phenyl group, C_6H_5, takes the place of a metal. Among the compounds of this class which phenol forms with organic acids, the following may be mentioned: —

Phenyl acetate, $C_8H_8O_2 (= CH_3 . CO_2 . C_6H_5)$. — This is formed by treating phenol with acetyl chloride.

NOTE FOR STUDENT. — What use is acetyl chloride put to as a reagent in organic chemistry? Explain its use. What conclusion can be drawn from the fact that acetyl chloride acts upon phenol, replacing one hydrogen by acetyl, C_2H_3O?

Substitution-products of phenol. Phenol is very susceptible to the action of various reagents, and a large number of substitution-products have been made from it.

Bromine acts upon it readily. If, for example, bromine water is added to a water solution of phenol, tri-brom-phenol is formed and precipitated.

Dilute nitric acid acts upon phenol, yielding two mono-nitro-phenols, $C_6H_4 \left\{\begin{matrix} NO_2 \\ OH \end{matrix}\right.$, one of which has been shown to belong to the ortho series, the other to the para series.

Experiment 67. Add 20g phenol to a mixture of 80cc water and 40cc ordinary concentrated nitric acid (sp. gr. 1.34). Stir, and, after a time, pour off the dilute acid from the oil. Wash with water, and then put it into a flask, with about a litre of water, arranged as shown in Fig. 15. Flask *A* holds nothing but water; while the oil, together with

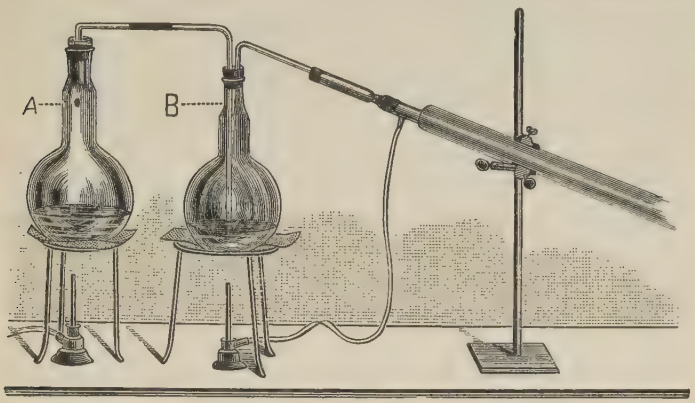


Fig. 15.

water, are in *B*. From *A* a current of steam is passed into *B*, which is heated by means of a lamp. Yellow crystals pass over and appear in the receiver, while a non-volatile substance remains behind in flask *B*. The volatile substance is ortho-nitro-phenol; the non-volatile is para-nitro-phenol.

Tri-nitro-phenol, picric acid, $C_6H_3N_3O_7\left(C_6H_2\left\{\begin{matrix}(NO_2)_3\\OH\end{matrix}\right.\right)$. This is formed very easily by the action of strong nitric acid on phenol.

Experiment 68. Add 10g phenol *slowly* to 10g concentrated nitric acid. When the action is over, add 30g fuming nitric acid and boil for some minutes. Extract the picric acid by means of hot water, and purify by dissolving in potassium carbonate, and evaporating to crystallization.

Picric acid crystallizes in yellow leaflets or prisms, has a very bitter taste (whence the name, from πικρός, bitter), is poisonous, decomposes with explosion when heated rapidly. It dyes wool and silk yellow.

NOTE FOR STUDENT. — Is there any analogy between tri-nitro-phenol and tri-nitro-glycerin? What is the essential difference between them?

It is extensively used as an explosive under the name *lyddite*.

One of the most interesting properties of tri-nitro-phenol is its power to form salts. It acts like a strong acid. It will thus be seen that, while the substance $C_6H_5.OH$ has only very slight acid properties, the same substance, with three of its hydrogens replaced by nitro groups, $C_6H_2(NO_2)_3.OH$, has strong acid properties. In the salts, which have the general formula $C_6H_2(NO_2)_3.OM$, the metals replace the hydrogen of the hydroxyl. Among them may be mentioned the potassium salt which was obtained in Exp. 68; this explodes when heated and when struck. *Ammonium picrate*, $C_6H_2(NO_2)_3.ONH_4$, is used as a constituent of explosives.

Aminophenols, $C_6H_4 < \begin{matrix} OH \\ NH_2 \end{matrix}$. — The aminophenols are formed by reducing the nitrophenols by means of tin and hydrochloric acid. Metaminophenol and some of its derivatives are used in the preparation of the *rhodamine dyes*.

Paraminophenol, a solid that melts at 184°, yields an ethyl ether, *p-phenetidine*, $C_6H_4 < \begin{matrix} OC_2H_5 \\ NH_2 \end{matrix}$. This ether is converted by glacial acetic acid into an acetyl derivative of the formula, $C_6H_4 < \begin{matrix} OC_2H_5 \\ NH.CO.CH_3 \end{matrix}$. This is sometimes called *acetaminophenetol*. It is extensively used in medicine under the name *phenacetin*.

Phenolsulphonic acids, $C_6H_4 < \begin{matrix} OH \\ SO_3H \end{matrix}$. — When phenol is treated with sulphuric acid, the ortho and para sulphonic acids are formed. At low temperatures the ortho acid is formed in larger quantity than the para acid. The ortho acid is readily converted into the para acid by heat, so that, at a comparatively high temperature, the para acid is the principal product. The change of the ortho acid to the para takes place even when its water solution is boiled. Orthophenolsulphonic acid is used in water solution as an antiseptic under the name *aseptol*.

Phenyl-mercaptan, Phenyl hydrosulphide, Thiophenol, $C_6H_6S(C_6H_5 . SH)$. — This bears the same relation to phenol that mercaptan bears to alcohol. It can be made by reducing benzene-sulphonic acid. This reduction is effected by first making the sulphon-chloride, $C_6H_5 . SO_2Cl$ (Exp. 64), and then treating this with nascent hydrogen.

Note for Student. — What is the effect of oxidizing the mercaptans?

It can be made, also, by treating phenol with phosphorus pentasulphide, the effect of this reagent being to substitute sulphur for oxygen.

Note for Student. — What analogy is there between the action of phosphorus pentachloride and of phosphorus pentasulphide on compounds containing oxygen?

Phenyl-mercaptan is a liquid, with a very disagreeable odor. It forms a crystallized mercury compound, $(C_6H_5S)_2Hg$.

Cresols, $C_7H_8O\left(C_6H_4 < \begin{matrix} CH_3 \\ OH \end{matrix}\right)$. — There are three cresols, or hydroxyl derivatives of toluene, of the formula $C_6H_4 < \begin{matrix} CH_3 \\ OH \end{matrix}$. They are all found in coal tar, and the tars from pine and beech wood. When mixed together, it is difficult to separate them. To obtain them in pure condition, it is therefore best to make them from the three toluidines, or from the three sulphonic acids of toluene.

Note for Student. — Give the equations representing the reactions involved in passing from the three toluidines to the cresols, and from the three toluene-sulphonic acids to the cresols.

The cresols resemble phenol very closely.

Creosote is a mixture of chemical compounds contained in wood tar. It contains the cresols. Coal-tar creosote consists largely of phenol.

Thymol, propyl-meta-cresol, $C_{10}H_{14}O\left(C_6H_3\left\{\begin{matrix}CH_3\\OH\ (m)\\C_3H_7(p)\end{matrix}\right.\right)$[1].

This phenol is contained in oil of thyme, together with cymene, and is made artificially from nitro-cuminic aldehyde, $C_6H_3\left\{\begin{matrix}CHO\\NO_2\ (m).\\C_3H_7(p)\end{matrix}\right.$ When this is reduced it gives an amino derivative of cymene, $C_6H_3\left\{\begin{matrix}CH_3\\NH_2\\C_3H_7\end{matrix}\right.$, which can be converted into thymol through the diazo compound. It forms large monoclinic crystals, which melt at 50°. It has a pleasant odor, like that of the oil of thyme. Treated with phosphorus pentoxide, it yields meta-cresol and propylene, C_3H_6; while, when treated with phosphorus pentasulphide, it yields cymene. These two reactions indicate that the groups contained in thymol bear to each other the relations indicated by the formula given above. It is one of the two theoretically possible hydroxyl derivatives of cymene. The other one, *carvacrol*, has the hydroxyl in the ortho position relatively to methyl. It has been made from the corresponding cymene-sulphonic acid; is found in nature in the ethereal oil of *Origanum hirtum;* and can be made from carvol, or the oil of caraway, by heating it with glacial phosphoric acid or with caustic potash.

Di-acid Phenols.

The three theoretically possible di-hydroxyl benzenes, $C_6H_4 < \begin{matrix}OH\\OH\end{matrix}$, are all well known.

[1] Formulas of this kind serve very well to indicate the relations of the groups and atoms contained in benzene derivatives. This one, for example, indicates that the hydroxyl is in the meta position (m) to methyl; while the propyl is in the para position to methyl (p). For di-substitution products, such formulas may also be used. Thus, the three toluidines may be represented by $C_6H_4 < \begin{matrix}CH_3\\NH_2(o)\end{matrix}$, $C_6H_4 < \begin{matrix}CH_3\\NH_2(m)\end{matrix}$, and $C_6H_4 < \begin{matrix}CH_3\\NH_2(p)\end{matrix}$.

Pyrocatechol, Ortho-di-hydroxy-benzene, $C_6H_6O_2\left(C_6H_4<\begin{matrix}OH\\OH_{(o)}\end{matrix}\right)$.

This substance is a frequent product of the dry distillation of natural substances, — as of catechu, morintannic acid, etc., — and of the melting of resins with caustic potash. It can be made by fusing ortho-chlor-phenol or ortho-phenol-sulphonic acid with caustic potash. It forms crystals, which melt at 104°. It is easily soluble in water, alcohol, and ether.

The dilute solution in water gives with ferric chloride a dark-green color, which becomes violet on the addition of a little of a very dilute solution of sodium carbonate.

It reduces silver nitrate in solution in cold water. It is used in photography.

Guaiacol, monomethyl pyrocatechol, $C_6H_4<\begin{matrix}OCH_3\\OH_{(o)}\end{matrix}$.

This substance was first found in guaiac resin. Hence its name. It is formed in considerable quantity in the distillation of wood, especially beech-wood. It is made synthetically by introducing methyl into pyrocatechol. Guaiacol is a liquid that solidifies at 28.5° and boils at 205°. The carbonate, $CO(OC_6H_4 . OCH_3)_2$, has been recommended as a remedy in tuberculosis.

Veratrol, dimethyl pyrocatechol, $C_6H_4<\begin{matrix}OCH_3\\OCH_3\end{matrix}$, is formed by treating the potassium salt of pyrocatechol with methyl iodide and by distilling *veratric acid*, $C_6H_3\begin{cases}CO_2H\\OCH_3\\OCH_3\end{cases}$, with lime.

Resorcinol, Meta-di-hydroxy-benzene, $C_6H_6O_2\left(=C_6H_4<\begin{matrix}OH\\OH_{(m)}\end{matrix}\right)$.

Resorcinol is formed by the melting of a number of resins with caustic potash, as of galbanum, sagapenum, asafœtida, etc. It is made, also, by melting meta-iodo-phenol or meta-benzene-disulphonic acid with caustic potash.

It crystallizes from water, usually in thick rhombic prisms. Melting-point, 118°.

With ferric chloride, the water solution gives a dark purple color. Heated for a few minutes with phthalic acid in a test-tube, a yellowish-red mass is formed. When this is added to dilute caustic soda, a wonderfully fluorescent solution is obtained. The explanation of this reaction will be given under the head of Tri-phenyl-methane, when the phthaleins will be described.

Resorcinol is used largely in the manufacture of certain dyes, and is therefore manufactured on the large scale.

Heated with sodium nitrite resorcinol gives a deep-blue dye. This is soluble in water and the solution is turned red by acids. It is called *lacmoid* and is used as an indicator.

Tri-nitro-resorcinol, Styphnic acid, $C_6H_3N_3O_8\left(C_6H\left\{\begin{matrix}(NO_2)_3\\(OH)_2\end{matrix}\right.\right)$.

This compound is formed by the action of nitric acid on resorcinol, and on those resins which give resorcinol when treated with caustic potash. It closely resembles picric acid. Heated with bromine and acetic acid, it yields the substance known as *brompicrin*, which has the formula $C(NO_2)Br_3$.

Hydroquinol, Para-di-hydroxy-benzene, $C_6H_6O_2\left(C_6H_4<\begin{matrix}OH\\OH_{(p)}\end{matrix}\right)$.

Hydroquinol is formed by the dry distillation of quinic acid, by reduction of quinone (which see), by means of sulphur dioxide, by fusing para-iodo-phenol with caustic potash, etc.

It is a crystallized substance which melts at 169°; easily soluble in alcohol, ether, and hot water.

Oxidizing agents, such as ferric chloride, chlorine, etc., convert it into quinone. It is used in photography as a "developer."

It would lead too far to discuss here the reactions which have been made use of for the purpose of determining to which series each of the three di-hydroxy-benzenes belongs. The principle involved, however, is simple. Either these substances must be converted, directly or indirectly, into others, in regard

to the relation of whose groups we have evidence; or substances, the relation of whose groups is known, must be converted into the di-hydroxy-benzenes. The reactions made use of for effecting the conversions are mainly those which have already been studied; viz., the formation of amino compounds from nitro compounds by reduction; the formation of diazo compounds from amino compounds; the formation of (1) hydroxyl derivatives, (2) chlorine, bromine, or iodine derivatives, from the diazo compounds; and the formation of hydroxyl derivatives from sulphonic acids.

Orcinol, Di-hydroxy-toluene, $\left.\right\} C_7H_8O_2 \left[C_6H_3 \left\{ \begin{matrix} CH_3 \\ OH_{(m)} \\ OH_{(m)} \end{matrix} \right. \right]$.

There are two dye-stuffs, known as *archil* and *litmus*, which are made from different lichens by exposing them in powdered condition in ammoniacal solution to the action of air. They are treated with decomposing urine, from which the ammonia is obtained. *Archil* contains a substance called *orcein*, which can be made from orcinol by treating it with ammonia. Orcinol is contained in several lichens. It is formed, also, by melting aloes with caustic potash, and by melting 1, 3, 5-chlor-toluene-sulphonic acid with caustic potash. The last reaction shows that orcinol is a di-hydroxy-toluene.

Orcinol crystallizes in large, colorless, monoclinic prisms. Turns red in the air. Ferric chloride turns the aqueous solution deep violet.

Treated with ammonia in moist air, it is converted into *orcein*, $C_{28}H_{24}N_2O_7$, a substance which dissolves in alkalies, forming beautiful red solutions.

Orcinol is manufactured on the large scale, and then converted into orcein, which is used as a dye.

Litmus is obtained from the lichens *Roccella* and *Lecanora* by treating them with ammonia and potassium carbonate. Commercial litmus is made by mixing the concentrated solution of the potassium salt with chalk or gypsum.

Tri-acid Phenols.

Pyrogallol, pyrogallic acid, Tri-hydroxy-benzene, $C_6H_6O_3[C_6H_3(OH)_3]$.

Pyrogallic acid is formed by dry distillation of gallic acid, the reaction being analogous to that by which benzene is produced by distillation of benzoic acid: —

$$\underset{\text{Benzoic acid.}}{C_6H_5.CO_2H} = \underset{\text{Benzene.}}{C_6H_6} + CO_2;$$

$$\underset{\text{Gallic acid.}}{C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases}} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

It is formed also when one of the chlor-phenol-sulphonic acids is fused with caustic potash: —

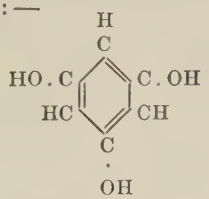
$$\underset{\text{Potassium chlor-phenol-sulphonate.}}{C_6H_3\begin{cases}OH\\Cl\\SO_3K\end{cases}} + \begin{matrix}KOH\\KOH\end{matrix} = \underset{\text{Pyrogallol.}}{C_6H_3\begin{cases}OH\\OH\\OH\end{cases}} + KCl + K_2SO_3.$$

It crystallizes in laminæ or needles; melts at 132–133°; is easily soluble in water, ether, and alcohol. In alkaline solution it absorbs oxygen rapidly and becomes brown. On account of this power to absorb oxygen it is used in gas analysis. It is poisonous. With a solution containing a ferrous and a ferric salt it gives a blue color.

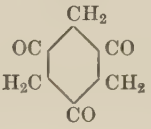
Most of the phenols give color reactions with ferric chloride, and most of them change color in the air. These changes in color are undoubtedly due to the action of oxygen. Towards oxidizing agents they are all unstable, most of them breaking down readily and yielding as the chief product of oxidation, carbon dioxide. In general, the larger the number of hydroxyl groups contained in a phenol, the less stable it is. We shall see that these same statements hold good for the hydroxy-acids of the benzene group, of which gallic acid and salicylic acid are examples.

Phloroglucinol, $C_6H_3(OH)_3$ $\left\{ C_6H_3 \left\{ \begin{matrix} OH\,(1) \\ OH\,(3) \\ OH\,(5) \end{matrix} \right. \right.$. — This phenol was first obtained from phloretin, which is one of the products of decomposition of a glucoside (see glucosides), phloridzin. It can be obtained also from other glucosides, and from several resins. Orcinol gives it when fused with potassium hydroxide, as does 1, 3, 5-benzene-trisulphonic acid.

In some of its reactions phloroglucinol acts like a trihydroxybenzene, in others it acts as if it contained three carbonyl groups, CO. In the present state of our knowledge we can only conclude that in contact with some reagents it actually is trihydroxybenzene, while in contact with others it is triketohexamethylene. The two conditions are represented by the formulas: —



Trihydroxybenzene.



Triketohexamethylene.

Many cases of this kind are known. The name *tautomerism* is given to this phenomenon. A substance that acts thus, as if it had two different structures, is said to appear in two tautomeric forms or to exhibit the phenomenon of tautomerism. It will be seen that in order that one form of phloroglucinol may be changed to the other a change in the position of three hydrogen atoms is necessary. Much attention is being given to phenomena of this kind at present.

Alcohols of the Benzene Series.

The phenols are those hydroxyl derivatives of the benzene hydrocarbons, which contain the hydroxyl in the place of one or more of the six benzene hydrogens. But just as there are

two classes of halogen substitution-products of toluene, in one of which the substitution has taken place in the benzene residue, and in the other in the marsh-gas residue, as indicated in the two formulas, —

$$C_6H_4Cl\,.\,CH_3 \quad \text{and} \quad C_6H_5\,.\,CH_2Cl,$$

so, also, there are two classes of hydroxyl derivatives: (1) the phenols, and (2) those in which the hydroxyl is in the marsh-gas residue. The simplest example of the second class corresponds to the formula, $C_6H_5\,.\,CH_2\,.\,OH$. It is isomeric with the cresols, $C_6H_4\,.\,OH\,.\,CH_3$, and has entirely different properties. While the cresols are the true homologues of phenol, the new substance is methyl alcohol in which one of the hydrogens of the methyl has been replaced by phenyl, C_6H_5. It may be represented by the formula, $C\begin{cases} C_6H_5 \\ H \\ H \\ OH \end{cases}$, when its analogy to ethyl alcohol, $C\begin{cases} CH_3 \\ H \\ H \\ OH \end{cases}$, is at once apparent.

Benzyl alcohol, $C_7H_8O(= C_6H_5.CH_2OH)$.—Benzyl alcohol or phenyl carbinol is found in nature in the balsams of Peru and Tolu, and in storax. In these substances it is, for the most part, in combination with benzoic or cinnamic acid. It is made by treating the oil of bitter almonds, which is the corresponding aldehyde, with nascent hydrogen: —

$$\underset{\text{Oil of bitter almonds.}}{C_6H_5.CHO} + H_2 = \underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2.OH}.$$

It is also made by replacing the chlorine in benzyl chloride, $C_6H_5.CH_2Cl$, by hydroxyl, just as methyl alcohol is made from methyl chloride by a similar replacement. In the case of benzyl chloride this can be effected even by boiling for a long time with water: —

$$C_6H_5.CH_2Cl + H_2O = C_6H_5.CH_2OH + HCl.$$

Benzyl alcohol is a colorless liquid with a pleasant odor. It boils at 206.5°. It dissolves with difficulty in water, and is soluble in alcohol and ether.

NOTE FOR STUDENT. — Notice the great difference between the boiling-point of methyl alcohol and that of phenyl-methyl alcohol.

Oxidizing agents convert the alcohol, first, into the oil of bitter almonds or benzoic aldehyde, and finally into benzoic acid. The relations between the three substances are like those between any primary alcohol and the corresponding aldehyde and acid, as shown by the formulas: —

$$\underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2OH}; \quad \text{or } \underset{\text{Benzoic aldehyde.}}{C_6H_5.CHO}; \quad \text{or } \underset{\text{Benzoic acid.}}{C_6H_5.CO_2H}.$$

Hydriodic acid converts benzyl alcohol into toluene: —

$$C_6H_5.CH_2OH + 2\,HI = C_6H_5.CH_3 + H_2O + 2\,I.$$

Benzyl alcohol conducts itself, in most respects, like the primary alcohols of the methyl alcohol series. A large number of its derivatives have been made and studied. Among them are *ethereal salts*, of which *benzyl acetate*, $CH_3.CO.OC_7H_7$, and *benzyl nitrate*, $NO_2.OC_7H_7$, may serve as examples; *ethers*, of which the *methyl ether*, $C_6H_5.CH_2.O.CH_3$, and the *phenyl ether*, $C_6H_5.CH_2.OC_6H_5$, are good examples; and *substitution-products*, of which *chlor-benzyl alcohol*, $C_6H_4Cl.CH_2OH$, and *nitro-benzyl alcohol*, $C_6H_4(NO_2).CH_2OH$, are examples.

These substitution-products are not made by direct treatment of the alcohol with the substituting agents, but by starting with the corresponding substituted toluene. Thus, chlor-benzyl alcohol is made from chlor-toluene, $C_6H_4Cl.CH_3$, by first converting this into chlor-benzyl chloride, $C_6H_4Cl.CH_2Cl$, and then replacing the chlorine of the group CH_2Cl by hydroxyl. By oxidation the substituted benzyl alcohols yield the corresponding substituted benzoic acids: —

$$C_6H_4Cl.CH_2OH + O_2 = \underset{\text{Chlor-benzoic acid.}}{C_6H_4Cl.CO_2H} + H_2O.$$

$$C_6H_4(NO_2).CH_2OH + O_2 = \underset{\text{Nitro-benzoic acid.}}{C_6H_4(NO_2)CO_2H} + H_2O.$$

Very few of the alcohols analogous to benzyl alcohol have been prepared. Plainly, the homologues may be of two kinds:

1. Those which are phenyl derivatives of the alcohols of the methyl alcohol series. Of this class, phenyl-ethyl alcohol, $C_6H_5.CH_2.CH_2OH$, the isomeric substance $C_6H_5.CH.OH.CH_3$, and phenyl-propyl alcohol, $C_6H_5.CH_2.CH_2.CH_2OH$, are examples. Phenyl-propyl alcohol is of special interest on account of its connection with cinnamic acid (which see), which has come into prominence since it has been shown to be closely related to the interesting substances of the indigo group. It occurs in storax in the form of an ethereal salt, which will be spoken of more fully under the head of Cinnamic Acid.

2. Those which are derivatives of xylene, mesitylene, etc., in the same sense that benzyl alcohol is a derivative of toluene. The following belong to this class: —

Tolyl-carbinol . . . . $C_6H_4 < \begin{matrix} CH_3 \\ CH_2OH \end{matrix}$,

and Cuminyl alcohol . . . . $C_6H_4 < \begin{matrix} CH_2OH \\ C_3H_{7(p)} \end{matrix}$,

which is made from cuminol, an aldehyde found in the oil of caraway.

Aldehydes of the Benzene Series.

The aldehydes of this group are closely related to the alcohols just considered. The simplest one is the oil of bitter almonds, or benzoic aldehyde, C_7H_6O.

Oil of bitter almonds, Benzoic aldehyde, $C_7H_6O(C_6H_5.CHO)$. — This substance occurs in combination in amygdalin, which is found in bitter almonds, laurel leaves, cherry kernels, etc. Amygdalin belongs to the class of bodies known as *glucosides*, which break up into a glucose and other substances. Amygdalin itself, under the influence of emulsin, which occurs with it in the

plants, breaks up into benzoic aldehyde, hydrocyanic acid, and dextrose: —

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2\,H_2O = \underset{\text{Benzoic aldehyde.}}{C_7H_6O} + CNH + \underset{\text{Glucose.}}{2\,C_6H_{12}O_6}.$$

Benzoic aldehyde can be made:

1. By oxidizing benzyl alcohol: —

$$C_6H_5 . CH_2OH + O = C_6H_5 . CHO + H_2O.$$

2. By distilling a mixture of calcium benzoate and calcium formate: —

$$\begin{array}{r} C_6H_5 . CO\boxed{OM} \\ H . \boxed{COOM} \end{array} = C_6H_5 . CHO + M_2CO_3.$$

3. By treating benzoyl chloride, the chloride of benzoic acid, with nascent hydrogen: —

$$C_6H_5 . COCl + H_2 = C_6H_5 . CHO + HCl.$$

4. By treating benzal chloride with water and milk of lime under pressure: —

$$C_6H_5 . CHCl_2 + H_2O = C_6H_5 . CHO + 2\,HCl.$$

NOTE FOR STUDENT. — Refer to the general methods for the preparation of aldehydes. Which of the above reactions are used for the preparation of aldehydes in general? Which of the reactions throw light upon the nature of aldehydes, and their relation to alcohols?

Benzoic aldehyde is prepared either from bitter almonds, which yield about 1.5 to 2 per cent; or from benzal chloride. On the large scale it is prepared by treating benzyl chloride with lead nitrate. The change is that represented in reaction 4 above.

Benzoic aldehyde is a liquid having a pleasant characteristic odor. It boils at 179°; is difficultly soluble in water; is not poisonous.

It unites with oxygen to form benzoic acid; with hydrogen to form benzyl alcohol; with hydrogen sulphide, ammonia, ammonium sulphide, alcohols, acids, anhydrides, and ketones.

In short, its powers of combination with other substances are almost unlimited. Hence, a very large number of derivatives are known.

Cuminic aldehyde, cuminol, $C_{10}H_{12}O\left(C_6H_4 < \begin{matrix} CHO \\ C_3H_{7(p)} \end{matrix}\right)$.

This aldehyde occurs in oil of caraway, from which it is made. It is a liquid with the odor of the oil of caraway. Its reactions are like those of benzoic aldehyde.

Benzaldoximes, $C_6H_5 \cdot CH{=}N \cdot OH$. — Hydroxylamine reacts with benzoic aldehyde as it generally reacts with aldehydes, forming an oxime: —

$$C_6H_5 \cdot CHO + H_2NOH = C_6H_5 \cdot CH{=}N \cdot OH + H_2O.$$

This appears first as an oil, but when purified it forms long, lustrous prisms, melting at 34°.

When hydrochloric acid gas is conducted into an ether solution of the above oxime, a hydrochloride is precipitated, and when this is treated with sodium carbonate, a new oxime, isomeric with the above, is obtained. This crystallizes from ether in thin, lustrous needles, and melts, when rapidly heated, at 128–130°. By continued heating, however, it is converted into the oxime, melting at 34°.

These two oximes are regarded as stereoisomeric. In terms of the conceptions of stereochemistry they should be represented by the formulas: —

$$C_6H_5-C-H \quad \text{and} \quad C_6H_5-C-H$$
$$\quad\quad\quad

[For an explanation of the significance of these formulas, especially as far as the nitrogen atom is concerned, see p. 290.]

The one with the hydrogen atom and the hydroxyl on opposite sides is called *benzantialdoxime;* the one with the hydrogen atom and the hydroxyl on the same side is called *benzsynaldoxime.* The one that melts at 128–130° easily loses water and forms phenyl cyanide or benzonitril, C_6H_5-CN. The other does not. It is believed that the one that loses water and yields the nitril is the synoxime. According to this the stable form, the one most easily obtained, is the antioxime. Phenomena of this kind have been extensively studied and the ideas here set forth rest upon a broad foundation of experimental evidence.

Acids of the Benzene Series.

The simplest of these acids is benzoic acid, which bears to benzene the same relation that acetic acid bears to marsh-gas. It is the carboxyl derivative of benzene. The homologous acids are derivatives of the homologous hydrocarbons. There are mono-basic, di-basic, tri-basic, and even hexa-basic acids, but the number actually known is small.

Monobasic Acids, $C_nH_{2n-8}O_2$.

Benzoic acid, $C_7H_6O_2(C_6H_5 \cdot CO_2H)$. — Benzoic acid occurs in gum benzoin, in the balsams of Peru and Tolu, and in combination with amino-acetic acid or glycine in the urine of herbivorous animals. It can be made in many ways, the most important of which are given below: —

1. By oxidation of benzyl alcohol or any alcohol which is a phenyl derivative of an alcohol of the methyl alcohol series. The common condition in all these alcohols is the presence of the difficultly oxidizable residue, C_6H_5, in combination with an easily oxidizable residue of an alcohol of the marsh-gas series: —

$C_6H_5 \cdot CH_2OH$	gives	$C_6H_5 \cdot CO_2H$;
$C_6H_5 \cdot CH_2 \cdot CH_2OH$	"	$C_6H_5 \cdot CO_2H$;
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	"	$C_6H_5 \cdot CO_2H$, etc.

2. By oxidation of benzoic aldehyde, and the aldehydes of the other alcohols referred to in the preceding paragraph.

3. By oxidation of all benzene hydrocarbons which contain but one residue of the marsh-gas series. Attention has already been called to this fact (see p. 265).

4. By treating cyan-benzene (phenyl cyanide, benzo-nitrile) with sulphuric acid (see Exp. 65, p. 294): —

$$C_6H_5CN + 2\,H_2O = C_6H_5.CO_2H + NH_3.$$

5. By treating benzene with carbonyl chloride in the presence of aluminium chloride: —

$$C_6H_6 + COCl_2 = C_6H_5.COCl + HCl;$$
$$C_6H_5.COCl + H_2O = C_6H_5.CO_2H + HCl.$$

A reaction similar to this is of extensive application in the preparation of some hydrocarbons. It will be treated of more fully under the head of Tri-phenyl-methane.

6. By treating benzene with carbon dioxide in the presence of aluminium chloride: —

$$C_6H_6 + CO_2 = C_6H_5.CO_2H.$$

This and the preceding methods are of special interest from the scientific point of view, for the reason that they clearly show the relation between benzoic acid, on the one hand, and benzene and carbonic acid, on the other.

NOTE FOR STUDENT. — Which of the methods above given are of general application for the preparation of the acids of carbon?

Benzoic acid is prepared on the large scale: (1) from gum benzoin by sublimation; (2) from the urine of horses and cows by treating the hippuric acid with hydrochloric acid; (3) from toluene, best, by converting it into benzyl chloride, and oxidizing this with dilute nitric acid.

Experiment 69. If the material is obtainable, evaporate a quantity of the urine of horses or cows to about one-half or one-third its vol-

ume. Add hydrochloric acid. On cooling, hippuric acid will be deposited. Recrystallize this several times from dilute nitric acid. Boil the hippuric acid for about a quarter of an hour with ordinary concentrated hydrochloric acid. By this means the hippuric acid is decomposed, yielding glycine (amido-acetic acid) and benzoic acid: —

$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + CH_2 < \underset{\text{Glycine.}}{\begin{matrix} NH_2 \\ CO_2H \end{matrix}}.$$

Benzoic acid forms lustrous laminæ or needles, which melt at 121°.

Experiment 70. Determine the melting-point of the benzoic acid which you have made from hippuric acid. If it is not as stated above, recrystallize from water until the melting-point is not changed by further crystallization. Those specimens which are least pure can be purified by recrystallizing them from dilute nitric acid.

The acid is comparatively easily soluble in hot water, but difficultly soluble in cold water. It is volatile with water vapor.

Experiment 71. Put some in a one-litre flask, with about 700cc to 800cc water. Connect with a condenser, and boil down to about 200cc. Neutralize the distillate with ammonia, and evaporate down to a small volume. Acidify, when benzoic acid will be thrown down.

Its vapor acts upon the mucous membrane of the respiratory passages, and causes coughing.

It sublimes very easily.

Experiment 72. Put some dry benzoic acid in a small, dry crystallizing dish, and put the dish in a sand-bath. Over the mouth of the dish put a paper cone made from filter-paper, arranged as shown in Fig. 16. Heat with a small flame. The benzoic acid will be deposited on the paper in beautiful lustrous needles.

Or another form of apparatus, which is useful for subliming small quantities of substance, consists, essentially, of two watch-glasses which are of exactly the same size. The edges of the glasses are ground to secure a good joint when they are brought together. In

using this apparatus, put the substance to be sublimed in one of the glasses; stretch a round piece of filter-paper over it, and then place the other glass upon it. Clamp the glasses together by means of a thin brass clamp. Now put the glasses on a sand-bath, and warm

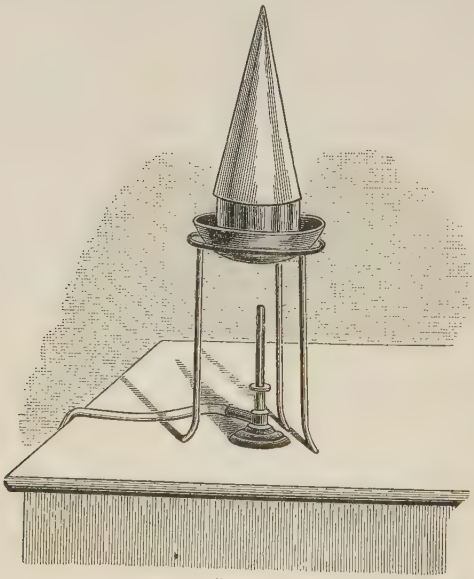


Fig. 16.

gently, when the substance will slowly pass through the paper and appear in crystals in the upper watch-glass. It is well to keep a small pad of moist filter-paper on the upper glass during the operation.

When heated with lime, benzoic acid breaks up into benzene and carbon dioxide (see Exp. 55) :—

$$C_7H_6O_2 = C_6H_6 + CO_2.$$

With sodium amalgam, it yields benzyl alcohol and other reduction-products. With hydriodic acid, it yields toluene, and then hydrogen addition-products of toluene.

A great many derivatives of benzoic acid are known.

Nearly all its salts are soluble in water.

The ethereal salts can be made by any of the general methods already described.

NOTE FOR STUDENT. — What are the general methods for the preparation of ethereal salts?

Experiment 73. Dissolve 40g benzoic acid in 150cc absolute alcohol. Pass *dry* hydrochloric acid gas into the solution, keeping the latter cool by surrounding it with water. When the solution is *saturated* with hydrochloric acid, connect the flask with an inverted condenser, and warm gently on a water-bath for half an hour. Now add three or four volumes of water, when ethyl benzoate will separate as an oil. Wash with water and a little sodium carbonate; and, finally, dry.

Benzoyl chloride, $C_6H_5 . COCl$, and *bromide*, $C_6H_5 . COBr$, are made from benzoic acid in the same way that acetyl chloride is made from acetic acid. They are more stable than the corresponding compounds of the fatty acids, but in general undergo the same kinds of change.

Benzoyl chloride acts upon hydroxyl compounds in the same general way that acetyl chloride does, and forms benzoyl compounds: —

$$C_6H_5 . OH + C_6H_5 . COCl = C_6H_5 . CO . O . C_6H_5 + HCl.$$

These benzoyl compounds are, as will be seen, esters of benzoic acid.

The reaction between hydroxyl compounds and benzoyl chloride is much aided by the addition of caustic potash.

Benzoyl cyanide, $C_6H_5 . CO . CN$, is made by distilling mercuric cyanide and benzoyl chloride: —

$$2\,C_6H_5 . COCl + Hg(CN)_2 = 2\,C_6H_5 . COCN + HgCl_2.$$

The cyanogen can be converted into carboxyl, and thus an acid of the formula $C_6H_5 . CO . CO_2H$ obtained. This is known as *benzoyl-formic* acid. It is of interest, for the reason that one of its derivatives is also a derivative of indigo (see Isatine).

Substitution-Products of Benzoic Acid.

Benzoic acid readily yields substitution-products when treated with the halogens, and with nitric and sulphuric acids. The products obtained by direct substitution belong mostly to the meta series. Thus, when chlorine acts upon benzoic acid, the main product is *meta-chlor-benzoic acid;* nitric acid gives mainly *meta-nitro-benzoic acid;* and sulphuric acid gives mainly *meta-sulpho-benzoic acid.*

NOTE FOR STUDENT. — Compare this with the result of the direct action of the same reagents on toluene. What are the first products of the action of nitric and sulphuric acids on toluene?

Substituted benzoic acids can be made, also, by oxidizing the corresponding substituted toluenes. Thus, chlor-toluene gives chlor-benzoic acid; nitro-toluene gives nitro-benzoic acid, etc.: —

$C_6H_4Cl.CH_3$ gives $C_6H_4Cl.CO_2H$;
$C_6H_4(NO_2)CH_3$ " $C_6H_4(NO_2)CO_2H$.

The three *nitro-benzoic acids* and the corresponding *amino-benzoic acids* may serve as examples of the mono-substitution products.

Ortho-nitro-benzoic acid, $C_7H_5NO_4\left(C_6H_4<\begin{matrix}CO_2H\\NO_{2(o)}\end{matrix}\right)$. — Ortho-nitro-benzoic acid is formed, together with a large quantity of the meta acid and some of the para acid, by treating benzoic acid with nitric acid, by oxidizing ortho-nitro-toluene with potassium permanganate, and by oxidizing ortho-nitro-cinnamic acid. It crystallizes in needles, melts at 147°, and has an intensely sweet taste.

Meta-nitro-benzoic acid, $C_6H_4<\begin{matrix}CO_2H\\NO_{2(m)}\end{matrix}$, is the chief product of the action of nitric acid on benzoic acid. It crystallizes in laminæ, or plates, and melts at 140° to 141°.

Para-nitro-benzoic acid, $C_6H_4<\begin{matrix}CO_2H\\NO_{2(p)}\end{matrix}$, is prepared best by oxidizing para-nitro-toluene. It crystallizes in laminæ,

melts at 238°, and is much less easily soluble in water than the ortho and meta acids.

The determination of the series to which these three acids belong is effected by transforming them into the amino-acids; and these, through the diazo compounds, into the corresponding hydroxy-acids of the formula $C_6H_4 < \begin{matrix} OH \\ CO_2H \end{matrix}$.

NOTE FOR STUDENT. — Give the equations representing the action involved in passing from toluene to ortho-hydroxy-benzoic acid (salicylic acid) by the method above referred to.

In a similar way, lines of connection can be established between the three hydroxy-acids and the chlor-, brom-, and iodo-benzoic acids.

NOTE FOR STUDENT. — What are the reactions?

The three hydroxy-acids, on the other hand, have been made by methods that connect them directly with the three dibasic acids of benzene, $C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$, which, in turn, have been made from the three xylenes.

Ortho-amino-benzoic acid, Anthranilic acid, } $C_7H_7NO_2\left(C_6H_4 < \begin{matrix} CO_2H \\ NH_{2(o)} \end{matrix}\right)$. — This acid is made by reducing ortho-nitro-benzoic acid with tin and hydrochloric acid, and by boiling indigo with caustic potash. It has already been stated that indigo yields aniline. Now, as ortho-amino-benzoic acid is also obtained, and this breaks up easily into aniline and carbon dioxide,

$$C_6H_4 < \begin{matrix} NH_2 \\ CO_2H \end{matrix} = C_6H_5.NH_2 + CO_2,$$

it seems probable that the aniline is a secondary product.

Like other amino acids, anthranilic acid is probably an inner salt and should, accordingly, be represented by the formula $C_6H_4 < \begin{matrix} CO_2 \\ NH_3 \end{matrix} >$. When it is diazotized it yields an inner diazonium salt of the formula $C_6H_4 < \begin{matrix} CO_2 \\ N \\ \| \\ N \end{matrix} >$.

Isatine, $C_8H_5NO_2\left(C_6H_4<\begin{matrix}CO\\N\end{matrix}>C.OH \text{ or } C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO\right)$. — Isatine is obtained by the oxidation of indigo, and from ortho-amino-benzoic acid as follows: —

The amino-acid is converted into the chloride, the chloride into the cyanide, and this into the corresponding carboxyl derivative, which is the ortho-amino derivative of benzoyl-formic acid. The ortho-amino-benzoyl-formic acid thus obtained loses water, and is converted into isatine. The changes are represented by these equations: —

(1) $C_6H_4<\begin{matrix}COOH\\NH_2(o)\end{matrix} + PCl_5 = C_6H_4<\begin{matrix}COCl\\NH_2(o)\end{matrix} + HCl + POCl_3;$

Ortho-amino-benzoic acid. Ortho-amino-benzoyl chloride.

(2) $C_6H_4<\begin{matrix}COCl\\NH_2(o)\end{matrix} + AgCN = C_6H_4<\begin{matrix}COCN\\NH_2(o)\end{matrix} + AgCl;$

Ortho-amino-benzoyl cyanide.

(3) $C_6H_4<\begin{matrix}COCN\\NH_2(o)\end{matrix} + 2\,H_2O = C_6H_4<\begin{matrix}COCOOH\\NH_2(o)\end{matrix} + NH_3;$

Ortho-amino-benzoyl-formic acid.

(4) $C_6H_4<\begin{matrix}CO.COOH\\NH_2(o)\end{matrix} = C_6H_4<\begin{matrix}CO\\N\end{matrix}>C.OH + H_2O,$

or $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO.$

Isatine.

The formula given for isatine represents it as an anhydride of ortho-amino-benzoyl-formic acid. The formation of anhydrides of aromatic acids is a characteristic of ortho compounds. Neither the meta nor para acids give up water. We shall find that this fact is illustrated in the case of the dibasic acids, the only one that yields an anhydride being ortho-phthalic acid, $C_6H_4<\begin{matrix}COOH\\COOH(o)\end{matrix}$, which gives phthalic anhydride, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$. This ready formation of anhydrides from ortho compounds, taken together with the fact that the meta and para compounds do not yield anhydrides, has been

regarded as an argument in favor of the view that in the ortho compounds the two substituting groups are actually nearer together than in the meta and para compounds.

Isatine illustrates the phenomenon of tautomerism (see page 309). Towards some reagents it reacts as though it contained hydroxyl; towards others as though it contained the imino group NH, as represented by the two formulas: —

$$C_6H_4 \left\langle \begin{matrix} CO \\ NH \end{matrix} \right\rangle CO \quad \text{and} \quad C_6H_4 \left\langle \begin{matrix} CO \\ N \end{matrix} \right\rangle\!\!\!\rangle C.OH.$$

The relation of isatine to indigo will be discussed briefly under the head of Indigo.

Meta- and Para-amino-benzoic acids are made from the corresponding nitro acids by reduction.

Hippuric acid, benzoyl-amino-acetic acid,
$C_9H_9NO_3 (= C_6H_5 . CONH . CH_2CO_2H)$.

Hippuric acid, as has already been seen (Exp. 69), occurs in the urine of herbivorous animals, as the cow, horse, camel, and sheep. Some hippuric acid is found in human urine under ordinary circumstances. If benzoic acid is taken with the food, it appears as hippuric acid in the urine, while derivatives of benzoic acid appear as derivatives of hippuric acid.

Hippuric acid can be made synthetically from benzoic acid and acetic acid:

1. By heating glycine with benzoic acid to 160°: —

$$C_6H_5 . CO \boxed{OH} + \boxed{H} \begin{matrix} HN \\ HO_2C \end{matrix} > CH_2 = CH_2 < \begin{matrix} NH . CO . C_6H_5 \\ CO_2H \end{matrix} + H_2O.$$

Hippuric acid.

2. By heating benzamide with chlor-acetic acid: —

$$C_6H_5 . CO . NHH + \begin{matrix} Cl \\ HO_2C \end{matrix} > CH_2 = \begin{matrix} C_6H_5 . CONH \\ HO_2C \end{matrix} > CH_2 + HCl.$$

Hippuric acid.

3. By heating glycine with benzoyl chloride: —

$$CH_2 < \begin{matrix} NHH \\ CO_2H \end{matrix} + Cl . OC . C_6H_5 = CH_2 < \begin{matrix} NH . CO . C_6H_5 \\ CO_2H \end{matrix} + HCl.$$

Hippuric acid crystallizes from water in long, rhombic prisms. It is decomposed into benzoic acid and glycine by boiling with alkalies, and more readily by boiling with dilute acids (Exp. 69): —

$$CH_2 < \begin{matrix} NH \cdot C_7H_5O \\ CO_2H \end{matrix} + H_2O = CH_2 < \begin{matrix} NH_2 \\ CO_2H \end{matrix} + C_6H_5 \cdot CO_2H.$$

Note for Student. — What relation does hippuric acid bear to benzamide? What is the effect of boiling acid amides with alkalies? Write the equation for the decomposition of benzamide, and compare it with that for the decomposition of hippuric acid.

Toluic acids, $C_8H_8O_2$. — There are four acids of this formula known; viz., the three carboxyl derivatives of toluene in which the carboxyl enters into the benzene ring, $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix}$, and an acid obtained from toluene by replacing a hydrogen of the methyl by carboxyl, thus, $C_6H_5 \cdot CH_2 \cdot CO_2H$. *Ortho-*, *meta-*, and *para-toluic acids*, $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix}$, are made by oxidizing the corresponding xylenes with nitric acid: —

$$C_6H_4 < \begin{matrix} CH_3 \\ CH_3 \end{matrix} + 3\,O = C_6H_4 < \begin{matrix} CO_2H \\ CH_3 \end{matrix} + H_2O.$$

They, as well as their derivatives, of which many are known, have been studied carefully. The substituted toluic acids can be made either by treating the acids with strong reagents or by oxidizing substituted xylenes: —

$$\underset{\text{Nitro-xylene.}}{C_6H_3(NO_2) < \begin{matrix} CH_3 \\ CH_3 \end{matrix}} + 3\,O = \underset{\text{Nitro-toluic acid.}}{C_6H_3(NO_2) < \begin{matrix} CO_2H \\ CH_3 \end{matrix}} + H_2O.$$

α-Toluic acid, Phenyl-acetic acid, $\Big\}$ $C_8H_8O_2(C_6H_5 \cdot CH_2 \cdot CO_2H)$. — Just as benzoic acid may be regarded as phenyl-formic acid, so α-toluic acid may be regarded as phenyl-acetic acid. It is obtained by reducing mandelic or phenyl-glycolic acid, $C_6H_5 \cdot CH(OH) \cdot CO_2H$, which is formed when amygdalin is treated with hydrochloric acid. It is prepared from toluene by converting this into benzyl chloride, from which the cyanide is made by boiling

with potassium cyanide. The cyanide is then treated with an alkali, and yields the acid: —

$$\underset{\text{Boiling toluene.}}{C_6H_5 . CH_3} + Cl_2 = \underset{\text{Benzyl chloride.}}{C_6H_5 . CH_2Cl} + HCl;$$

$$C_6H_5 . CH_2Cl + KCN = \underset{\text{Benzyl cyanide.}}{C_6H_5 . CH_2CN} + KCl;$$

$$C_6H_5 . CH_2CN + 2\,H_2O = \underset{\text{α-Toluic acid.}}{C_6H_5 . CH_2 . CO_2H} + NH_3.$$

The acid crystallizes in thin laminæ; and melts at 76.5°.

Note for Student. — What would you expect α-toluic acid to yield when oxidized? (See p. 265.) What would you expect it to yield when distilled with lime? What would you expect the three toluic acids, $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix}$, to yield by oxidation, and when distilled with lime? (See p. 318.)

Oxindol, $C_8H_7NO\left(C_6H_4 < \begin{matrix} CH_2 \\ NH \end{matrix} > CO, \text{ or } C_6H_4 < \begin{matrix} CH_2 \\ N \end{matrix} \geqslant C.OH\right)$. — Oxindol is obtained by reduction of isatine (see p. 322); and also from ortho-amino-α-toluic acid by loss of water, in the same way that isatine is formed from ortho-amino-benzoyl-formic acid. When α-toluic acid is treated with nitric acid, the para- and ortho-nitro acids are formed. The latter is reduced by means of tin and hydrochloric acid, when oxindol is at once obtained: —

$$\underset{\text{Ortho-amino-α-toluic acid.}}{C_6H_4 < \begin{matrix} CH_2 . COOH \\ NH_{2(o)} \end{matrix}} = \underset{\text{Oxindol.}}{C_6H_4 < \begin{matrix} CH_2 \\ NH \end{matrix} > CO} + H_2O.$$

Mesitylenic acid, $C_9H_{10}O_2\left(= C_6H_3 \left\{ \begin{matrix} (CH_3)_2 \\ CO_2H \end{matrix} \right.\right)$. — This acid has already been referred to as the first product of oxidation of mesitylene. It is the only monobasic acid that has been obtained from mesitylene; and, according to the accepted hypothesis, it is the only one possible. By distillation with lime, it yields meta-xylene. Further oxidation converts it into uvitic and trimesitic acids (see p. 265).

Note for Student. — Of what special significance is the formation of meta-xylene from mesitylenic acid?

Hydro-cinnamic acid, Phenyl-propionic acid, $C_9H_{10}O_2(C_6H_5.CH_2.CH_2.CO_2H)$. — Hydro-cinnamic or phenyl-propionic acid is obtained by treating cinnamic acid with nascent hydrogen: —

$$\underset{\substack{\text{Cinnamic acid,}\\ \beta\text{-Phenyl-acrylic acid.}}}{C_6H_5.CH:CH.CO_2H} + H_2 = \underset{\substack{\text{Hydro-cinnamic acid,}\\ \beta\text{-Phenyl-propionic acid.}}}{C_6H_5.CH_2.CH_2.CO_2H}.$$

It is also made by starting with ethyl-benzene, $C_6H_5.C_2H_5$, and using the same reactions that are necessary to transform toluene into α-toluic acid (see p. 324). It is a product of the decay of several animal substances, such as albumin, fibrin, brain, etc. It crystallizes from water, in long needles, which melt at 47°. It yields benzoic acid when oxidized.

Ortho-amino-hydro-cinnamic acid, $C_6H_4 < \begin{matrix} CH_2.CH_2.CO_2H \\ NH_{2(o)} \end{matrix}$. — This acid is prepared from hydro-cinnamic acid in the same way that ortho-amino-α-toluic acid is made from α-toluic acid. It is not obtained in the free state; but, like the ortho-amino derivatives of benzoyl-formic and of α-toluic acids, it loses water, and forms the anhydride.

Hydro-carbostyril, $C_6H_4 < \begin{matrix} C_2H_4 \\ NH \end{matrix} > CO$. — Hydro-carbostyril is made by treating ortho-nitro-hydro-cinnamic acid with tin and hydrochloric acid. It is a solid which crystallizes in prisms, melting at 160°. It is interesting chiefly for the reason that it is closely related to the important compound *quinoline* (which see). When treated with phosphorus pentachloride, hydro-carbostyril is converted into di-chlor-quinoline. The significance of this reaction will appear later.

Dibasic Acids, $C_nH_{2n-10}O_4$.

The simplest acids of this group are the three phthalic acids, which are the di-carboxyl derivatives of benzene, belonging to the ortho, meta, and para series.

Phthalic acid, Ortho-phthalic acid, $C_8H_6O_4\left(=C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}\right)$. — Phthalic acid was the first of the three acids of this composition dis-

covered; and, as it was obtained from naphthalene, it was named phthalic acid. It is manufactured on the large scale by oxidizing naphthalene by means of sulphuric acid. It can further be formed from alizarin and purpurin; and from ortho-toluic acid, $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H_{(o)} \end{matrix}$, by oxidation with potassium permanganate.

Experiment 74. Mix 40g naphthalene and 80g potassium chlorate, and add this mixture *gradually* to 400g ordinary concentrated hydrochloric acid. Naphthalene tetra-chloride, $C_{10}H_8 . Cl_4$, is formed in this reaction. Wash with water. *Gradually* add 400g ordinary concentrated nitric acid (sp. gr. 1.45), and boil in a large retort with upright neck. When all is dissolved, evaporate the nitric acid; and, finally, distil the residue. Phthalic anhydride passes over. Recrystallize from water. This will be used for other experiments.

Phthalic acid forms rhombic crystals, which melt at 213° or lower, according to circumstances, as, when heated, it breaks up gradually, even below the melting-point, into water and the anhydride which melts at 128°. Distilled with lime, it yields benzene; though, by selecting the right proportions, benzoic acid can be obtained: —

(1) $$C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = C_6H_6 + 2\,CO_2;$$

(2) $$C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = C_6H_5 . CO_2H + CO_2.$$

Phthalic acid is decomposed by chromic acid, yielding only carbon dioxide and water. Hence, ortho-xylene, when treated with chromic acid, does not yield phthalic acid. By boiling ortho-xylene with nitric acid, however, it yields ortho-toluic acid, $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H_{(o)} \end{matrix}$, and this can be oxidized to phthalic acid by treatment with potassium permanganate.

Phthalic anhydride, $C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > O$, is formed by heating phthalic acid. It forms long needles, which melt at 128°. Heated with phenols, it forms the compounds known as *phthaleïns* (which see).

Isophthalic acid, Meta-phthalic acid, $\left.\begin{matrix}\\ \\ \end{matrix}\right\} C_6H_4 < \begin{matrix} CO_2H \\ CO_2H_{(m)} \end{matrix}$, is formed by oxidizing either meta-xylene or meta-toluic acid with chromic acid; by distilling meta-benzene-disulphonic acid with potassium cyanide, and boiling the resulting dicyanide with an alkali.

NOTE FOR STUDENT. — Write the equations representing the action involved in passing from meta-benzene-disulphonic acid to isophthalic acid. Into which dihydroxy-benzene is this same disulphonic acid converted by melting it with caustic potash?

The acid is formed, further, by treating meta-sulpho-benzoic acid with sodium formate: —

$$C_6H_4 < \begin{matrix} CO_2K \\ SO_3K(m) \end{matrix} + H.CO_2Na = C_6H_4 < \begin{matrix} CO_2K \\ CO_2K(m) \end{matrix} + HNaSO_3.$$

Potassium sulpho-benzoate. — Potassium iso-phthalate.

This reaction is of importance, for the reason that the same sulpho-benzoic acid, which is thus converted into isophthalic acid, can also be converted into one of the three hydroxy-benzoic acids; and thus connection is established between the latter and isophthalic acid and meta-xylene.

Isophthalic acid crystallizes in fine needles from water. It melts above 300°, and is not converted into an anhydride.

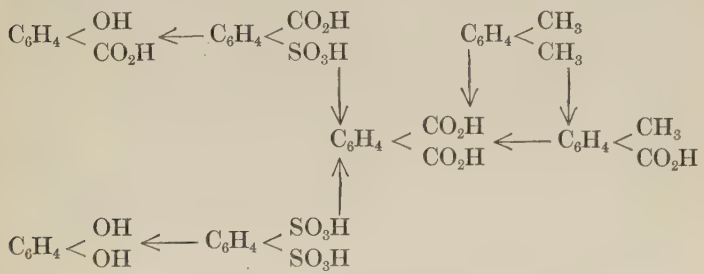
Terephthalic acid, Para-phthalic acid, $\left.\begin{matrix}\\ \\ \end{matrix}\right\} C_6H_4 < \begin{matrix} CO_2H \\ CO_2H_{(p)} \end{matrix}$. — Terephthalic acid is formed by oxidation of the oil of turpentine,[1] cymene, para-xylene, and para-toluic acid; by heating a mixture of potassium para-sulpho-benzoate and sodium formate: —

$$C_6H_4 < \begin{matrix} CO_2K \\ SO_3K(p) \end{matrix} + H.CO_2Na = C_6H_4 < \begin{matrix} CO_2K \\ CO_2K(p) \end{matrix} + HNaSO_3.$$

Potassium para-sulpho-benzoate. — Potassium tere-phthalate.

[1] The prefix *tere* is derived from the Latin *terebinthinus*, turpentine.

Para-sulpho-benzoic acid is converted into one of the three hydroxy-benzoic acids by caustic potash. In the para as well as the meta series, the lines of connection indicated below have been established: —



Terephthalic acid is a solid which is practically insoluble in water. It sublimes without melting and, like isophthalic acid, yields no anhydride.

Hexabasic Acid.

Mellitic acid, $C_{12}H_6O_{12}[= C_6(CO_2H)_6]$. — This acid occurs in nature in the form of the aluminium salt, as the mineral *honey-stone* or *mellite*. The mineral is rare, and is found in beds of lignite. Mellitic acid has been made by direct oxidation of carbon with potassium permanganate, and by oxidation of hexa-methyl-benzene, $C_6(CH_3)_6$. By ignition with soda-lime it is converted into benzene and carbon dioxide: —

$$C_6(CO_2H)_6 = C_6H_6 + 6\,CO_2.$$

Phenol-acids, or Hydroxy-acids of the Benzene Series.

It will be remembered that the alcohol acids or hydroxy-acids of the paraffin series form an important class, including such compounds as glycolic, lactic, malic, tartaric, and citric acids. The peculiarity of these compounds is their double character. They are at the same time alcohols and acids, though the acid properties are more prominent than the alco-

holic. The hydroxy-acids of the benzene series bear the same relations to the benzene hydrocarbons that the hydroxy-acids already studied bear to the paraffins. The simplest are those which contain one hydroxyl and one carboxyl in benzene, having the formula $C_6H_4 < \begin{matrix} OH \\ CO_2H \end{matrix}$.

Mono-hydroxy-benzoic Acids, $C_7H_6O_3$.

Salicylic acid, Ortho-hydroxy-benzoic acid, $\Big\}$ $C_6H_4 < \begin{matrix} OH \\ CO_2H^{(o)} \end{matrix}$. — Salicylic acid is found in the form of an ethereal salt of methyl, in the oil of wintergreen, prepared from the blossoms of *Gaultheria procumbens*. It is formed in a number of ways, among which the following should be specially mentioned: —

1. By converting ortho-amino-benzoic acid into the diazo compound, and boiling with water (see p. 286).

Note for Student. — Give the equations representing the reactions.

2. By melting ortho-sulpho-benzoic acid with caustic potash.

Note for Student. — Write the equation.

3. By treating sodium phenolate with carbon dioxide. The sodium salt is first saturated with carbon dioxide under pressure in closed vessels. This gives sodium phenyl carbonate, $C_6H_5 . O . CO . ONa$. By heating this to 120–130° under pressure it is converted into sodium salicylate: —

$$C_6H_5 . O . CO . ONa = C_6H_4 < \begin{matrix} OH \\ CO_2Na \end{matrix}.$$

4. By heating phenol with tetra-chlor-methane and alcoholic potash: —

$$C_6H_5 . OH + CCl_4 + 6\,KOH = C_6H_4 < \begin{matrix} OK \\ CO_2K \end{matrix} + 4\,KCl + 4\,H_2O.$$

5. By saponifying the methyl salicylate found in oil of wintergreen: —

$$C_6H_4 < \begin{matrix} OH \\ CO_2CH_3 \end{matrix} + KOH = C_6H_4 < \begin{matrix} OH \\ CO_2K \end{matrix} + CH_3OH.$$

Experiment 75. Boil 30cc to 40cc oil of wintergreen with moderately strong caustic potash in a flask connected with an inverted condenser. When it is dissolved, acidify with hydrochloric acid. Filter off the salicylic acid which separates, and recrystallize from water.

Experiment 76. Dissolve 80g sodium hydroxide and 40g phenol in 130cc water in a litre flask, arranged as in Fig. 17. If the mixture is cool, heat to 50–60°, and remove the flame. *Slowly* add 60g chloroform, shaking the mixture for several minutes after each addition. The mixture gradually becomes dark colored. An hour or more may be required

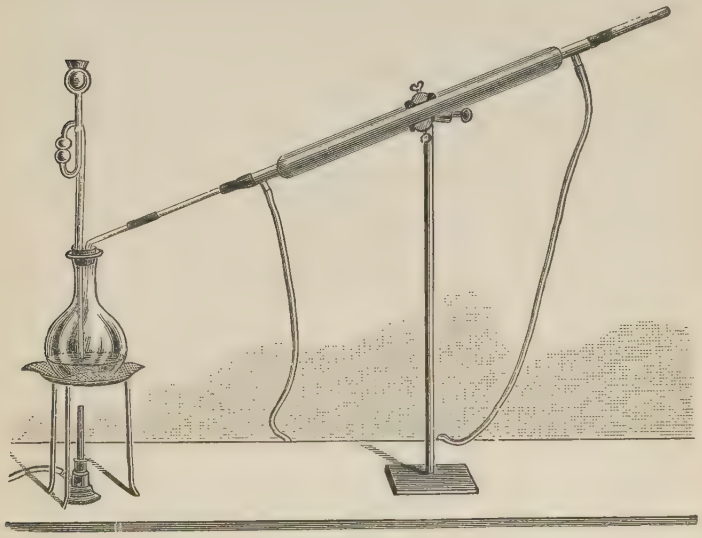


Fig. 17.

to complete the addition of all the chloroform. When the action is over, boil for an hour, and then distil off the excess of chloroform on the water-bath. Acidify with dilute hydrochloric acid, when a thick reddish brown oil comes down. Distil in steam as in Exp. 67, until the distillate no longer appears in milky drops. A light-colored oil consisting of salicylic aldehyde and phenol settles in the receiver. Decant the supernatant water. Extract with ether, and concentrate the extract by evaporation in a water-bath. To the concentrated extract add a saturated solution of mono-sodium sulphite (freshly prepared by dissolving

40g sodium sulphite in 75cc hot water, cooling the solution, and saturating with sulphur dioxide). Shake the mixture 8 or 10 times, 2 or 3 minutes at a time, for half an hour; then allow it to stand for several hours. The aldehyde unites with the sulphite, forming small, glistening, white crystals, while the phenol remains in solution in the ether. Filter with the aid of a pump, and wash the crystals with alcohol. Then treat the crystals on the water-bath with hydrochloric acid, when salicylic aldehyde is thrown down. Extract completely with ether, separate the two solutions, and evaporate the ether.

In an iron or silver dish, melt 25g caustic potash; remove the lamp; and add the salicylic aldehyde drop by drop, stirring constantly. The potassium salt of salicylic acid is thus formed. After the mass is cooled, dissolve in water, and precipitate the salicylic acid with dilute hydrochloric acid. Filter, wash with cold water, and purify by recrystallizing from water.

The action of chloroform on phenol in the presence of caustic soda is analogous to that of tetra-chlor-methane. It will be understood with the aid of the following equations: —

(1) $$C_6H_5.OH + CHCl_3 = C_6H_4{<}\begin{matrix}OH\\CHCl_2\end{matrix} + HCl;$$

(2) $$C_6H_4{<}\begin{matrix}OH\\CHCl_2\end{matrix} + 2\,NaOH = C_6H_4{<}\begin{matrix}OH\\CH(OH)_2\end{matrix} + 2\,NaCl;$$

(3) $$C_6H_4{<}\begin{matrix}OH\\CH(OH)_2\end{matrix} = C_6H_4{<}\begin{matrix}OH\\CHO\end{matrix} + H_2O.$$

This reaction is of general application to phenols, and affords a very convenient method for the preparation of the phenol-aldehydes and from these the acids.

Salicylic acid crystallizes from hot water in fine needles. It melts at 155° to 156°.

When heated with soda-lime, it breaks up into phenol and carbon dioxide: —

$$C_6H_4{<}\begin{matrix}OH\\CO_2H\end{matrix} = C_6H_5.OH + CO_2.$$

Heated alone it gives phenyl salicylate (salol) and xanthone: —

(1) $2C_6H_4<\begin{matrix}OH\\COOH\end{matrix} = C_6H_4<\begin{matrix}OH\\COOC_6H_5\end{matrix} + CO_2 + H_2O;$

Phenyl salicylate (salol).

(2) $C_6H_4<\begin{matrix}OH\\COOC_6H_5\end{matrix} = C_6H_4<\begin{matrix}O\\CO\end{matrix}> C_6H_4 + H_2O.$

Xanthone.

With ferric chloride, its aqueous solution gives a characteristic dark violet-blue color. Free salicylic acid is antiseptic, preventing decay and fermentation. It is therefore used for preserving foods. It is also used extensively in medicine, especially in rheumatism.

Salicylic acid forms salts of the general formula $C_6H_4<\begin{matrix}OH\\CO_2M\end{matrix}$; and, with the alkalies, compounds, in which both the phenol hydrogen and the acid hydrogen are replaced by metals, as $C_6H_4<\begin{matrix}OK\\CO_2K\end{matrix}$. Salts of the latter order, which contain the metals of the alkaline earths, are decomposed by carbon dioxide. The basic calcium salt, $C_6H_4<\begin{matrix}O\\CO_2\end{matrix}> Ca + H_2O$, is very difficultly soluble in water. Salicylic acid forms ethereal salts of the general formula $C_6H_4<\begin{matrix}OH\\CO_2R\end{matrix}$, of which methyl salicylate, $C_6H_4<\begin{matrix}OH\\CO_2CH_3\end{matrix}$, is the best-known example. It forms, also, ether-acids of the general formula $C_6H_4<\begin{matrix}OR\\CO_2H\end{matrix}$; and, finally, compounds of the general formula $C_6H_4<\begin{matrix}OR\\CO_2R\end{matrix}$.

A very large number of substitution-products and other derivatives of salicylic acid have been studied.

Phenyl salicylate (salol), $C_6H_4<\begin{matrix}OH\\COOC_6H_5\end{matrix}$. — This is formed when salicylic acid is heated alone to 200–220°, and when salicylic acid, phenol, and phosphorus oxychloride are heated together. It is a solid that melts at 43°. It is extensively used as an antiseptic.

That salicylic acid belongs to the ortho series, follows from the following facts: —

Ortho-toluene-sulphonic acid has been converted into ortho-sulpho-benzoic acid, and this into salicylic acid. Further, the same toluene-sulphonic acid has been converted into ortho-toluic acid, which, by oxidation, yields phthalic acid.

(1) $C_6H_4 < \begin{matrix} CH_3 \\ SO_3H_{(o)} \end{matrix} + 3\,O = C_6H_4 < \begin{matrix} CO_2H \\ SO_3H_{(o)} \end{matrix} + H_2O;$

Ortho-toluene-sulphonic acid. Ortho-sulpho-benzoic acid.

(2) $C_6H_4 < \begin{matrix} CO_2K \\ SO_3K_{(o)} \end{matrix} + KOH = C_6H_4 < \begin{matrix} CO_2K \\ OH_{(o)} \end{matrix} + K_2SO_3;$

Potassium salicylate.

(3) $C_6H_4 < \begin{matrix} CH_3 \\ SO_3K_{(o)} \end{matrix} + KCN = C_6H_4 < \begin{matrix} CH_3 \\ CN_{(o)} \end{matrix} + K_2SO_3;$

(4) $C_6H_4 < \begin{matrix} CH_3 \\ CN \end{matrix} + 2\,H_2O = C_6H_4 < \begin{matrix} CH_3 \\ CO_2H_{(o)} \end{matrix} + NH_3;$

Ortho-toluic acid.

(5) $C_6H_4 < \begin{matrix} CH_3 \\ CO_2H_{(o)} \end{matrix} + 3\,O = C_6H_4 < \begin{matrix} CO_2H \\ CO_2H_{(o)} \end{matrix} + H_2O.$

Phthalic acid.

Oxybenzoic acid, Meta-hydroxy-benzoic acid, $\Big\}\ C_6H_4 < \begin{matrix} OH \\ CO_2H_{(m)} \end{matrix}$. — This acid is made from meta-amino-benzoic and meta-sulpho-benzoic acid by the usual reactions.

It crystallizes from water in needles united to form wart-like-looking masses. It gives no color with ferric chloride. Its connection with meta-phthalic (isophthalic) acid and meta-xylene is shown by means of the transformations tabulated on p. 329; that is to say, the same sulpho-benzoic acid which, by melting with caustic potash, yields oxybenzoic acid, by melting with sodium formate, yields isophthalic acid. Therefore oxybenzoic acid is a meta compound.

Para-oxybenzoic acid, Para-hydroxy-benzoic acid, $\Big\}\ C_6H_4 < \begin{matrix} OH \\ CO_2H_{(p)} \end{matrix}$. — Para-oxy-benzoic acid is formed from the corresponding amino and

sulpho-benzoic acids; by treating various resins with caustic potash; from anisic acid (which see), by heating with hydriodic acid; by heating potassium phenolate in a current of carbon dioxide to 220°.

NOTE FOR STUDENT. — Notice the fact that, while *sodium* phenolate, when heated in a current of carbon dioxide, yields salicylic acid, *potassium* phenolate, under the same circumstances, yields para-oxybenzoic acid.

Its aldehyde is formed, together with salicylic aldehyde, by treating phenol with chloroform and caustic soda (see Exp. 76).

The reasons for regarding para-oxybenzoic acid as a member of the para series are similar to those which show that oxybenzoic acid is a meta compound. The same sulpho-benzoic acid that yields para-oxybenzoic acid, also yields terephthalic acid.

Anisic acid, Para-methoxy-benzoic[1] acid, $\left.\begin{matrix}\\ \\ \end{matrix}\right\} C_6H_4 < \begin{matrix}OCH_3 \\ CO_2H_{(p)}\end{matrix}$. — Anisic acid is formed by the oxidation of anethol, $C_6H_4 < \begin{matrix}OCH_3 \\ C_3H_5\end{matrix}$, a phenol ether contained in anise oil. It is made by heating para-oxybenzoic acid with caustic potash and methyl iodide and saponifying the di-methyl ether thus formed. As the formula indicates, it is the methyl ether of para-oxybenzoic acid. As will be seen, it is isomeric with methyl salicylate. By boiling with caustic alkali the latter is saponified, while anisic acid is not. When anisic acid is distilled with lime anisol is formed.

DI-HYDROXY-BENZOIC ACIDS, $C_7H_6O_4$.

Protocatechuic acid, $C_6H_3 \left\{ \begin{matrix}(OH)_2 \\ CO_2H\end{matrix}\right.$, is a frequent product of the fusion of organic substances with caustic potash. Thus, the following substances, among others, yield it: oil of cloves, piperic acid, catechin, gum benzoin, asafœtida, vanillin, etc.

[1] *Methoxy* is derived from *methoxyl*, the name given to the ether group, OCH_3. In a similar way OC_2H_5 is called *ethoxyl*; OC_6H_5, *phenoxyl*, etc.

It is made from sulpho-oxybenzoic acid, and from sulpho-para-oxybenzoic acids by fusing with caustic potash.

NOTE FOR STUDENT. — What analogy is there between the fact that protocatechuic acid is formed from sulpho-oxybenzoic acid and from sulpho-para-oxybenzoic acid, and the fact that pseudocumene is formed from brom-meta-xylene and from brom-para-xylene? What conclusion may be drawn regarding the relations of the two hydroxyl groups, and the carboxyl in protocatechuic acid?

By distillation with lime, protocatechuic acid breaks up into pyrocatechol and carbon dioxide: —

$$C_6H_3\begin{cases}OH\\OH\\CO_2H\end{cases} = C_6H_4\underset{\text{Pyrocatechol.}}{\begin{cases}OH\\OH\end{cases}} + CO_2.$$

Vanillic acid, $C_6H_3\begin{cases}OCH_3\\OH\\CO_2H\end{cases}$, is formed by oxidation of vanillin, which is the corresponding aldehyde. It is the monomethyl ether of protocatechuic acid.

Vanillin, $C_3H_8O_3\left(C_6H_3\begin{cases}OCH_3\\OH\\CHO\end{cases}\right)$, is the active constituent of the vanilla bean. It is made artificially by treating the ether, guaiacol, $C_6H_4<\begin{matrix}OCH_3\\OH_{(O)}\end{matrix}$, with chloroform and caustic soda.

Piperonal, $C_6H_3\begin{cases}CHO\\O\\O\end{cases}>CH_2$. — This is formed by oxidizing piperic acid, which is itself a product of the decomposition of piperine, a complex compound that is found in different varieties of pepper. Piperonal is the methylene ether of protocatechuic aldehyde. It can be made artificially, and is used in perfumery under the name *heliotropine*. The relations between protocatechuic aldehyde, vanillin, and piperonal are shown by the following formulas: —

$C_6H_3\begin{cases}CHO\ (1)\\OH\ (3)\\OH\ (4)\end{cases}$ Protocatechuic aldehyde.

$C_6H_3\begin{cases}CHO\ (1)\\OCH_3\ (3)\\OH\ (4)\end{cases}$ Vanillin.

$C_6H_3\begin{cases}CHO\ (1)\\O\\O>CH_2\ (3)\ (4)\end{cases}$ Piperonal (Heliotropine).

Tri-hydroxy-benzoic Acids, $C_7H_6O_5$.

Gallic acid, $C_7H_6O_5 + H_2O\left(C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases}\right)$. — Gallic acid occurs in sumach, in Chinese tea, and in many other plants. It is formed by boiling tannin or tannic acid with dilute sulphuric acid; by melting brom-protocatechuic acid with caustic potash: —

$$C_6H_2\begin{cases}Br\\(OH)_2\\CO_2H\end{cases} + KOH = C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases} + KBr.$$

Brom-protocatechuic acid. Gallic acid.

It is best prepared from gall nuts by fermentation of the tannin contained in them.

Gallic acid is difficultly soluble in cold water, easily in hot water, alcohol, and ether. Its solution gives, with a little ferric chloride solution, a blue-black precipitate, which dissolves in excess of ferric chloride, forming a dark green solution. It readily reduces gold and silver salts in solution. When distilled, it yields pyrogallol (pyrogallic acid) and carbon dioxide: —

$$C_6H_2\begin{cases}(OH)_3\\CO_2H\end{cases} = C_6H_3(OH)_3 + CO_2.$$

Tannic acid, tannin, $C_{14}H_{10}O_9$. — This substance occurs in gall nuts, from which it is extracted in large quantities. It is an amorphous powder. It is markedly astringent in its action on the mucous membranes. It is soluble in water, the solution giving, with ferric chloride, a dark blue-black color. Tannin is used extensively in medicine, in dyeing, and in the manufacture of ink and leather. It combines with gelatin forming an

insoluble substance. Its relation to gallic acid is indicated by the following equation: —

$$\underset{\text{Gallic acid.}}{2\,C_7H_6O_5} = \underset{\text{Tannin.}}{C_{14}H_{10}O_9} + H_2O.$$

Ketones and allied Derivatives of the Benzene Series.

The ketones of the benzene series are strictly analogous to those of the paraffin series, and they are made in the same way. Acetone is made by distilling calcium acetate: —

$$\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\rangle O + Ca = \underset{\text{Acetone.}}{\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO} + CaCO_3.$$

So, also, benzophenone or diphenyl-ketone is made by distilling calcium benzoate: —

$$\left.\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}\right\rangle O + Ca = \underset{\text{Benzophenone.}}{\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\rangle CO} + CaCO_3.$$

Further, by distilling mixtures of the salts of two fatty acids, mixed ketones are obtained: —

$$\begin{matrix}CH_3.CO\\C_2H_5.CO\end{matrix}\Big|OM\Big| = \underset{\substack{\text{Ethyl-methyl}\\\text{ketone.}}}{\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CO} + M_2CO_3.$$

And, similarly, mixed ketones containing one residue of a benzene hydrocarbon and one of a paraffin; or, two different residues of benzene hydrocarbons can be obtained thus: —

(1) $$\begin{matrix}C_6H_5.COOM\\CH_3.COOM\end{matrix} = \underset{\substack{\text{Phenyl-methyl ketone,}\\\text{Acetophenone.}}}{\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\rangle CO} + M_2CO_3;$$

(2) $$\begin{matrix}C_6H_5.COOM\\C_6H_4<\begin{matrix}CH_3\\COOM\end{matrix}\end{matrix} = \underset{\text{Phenyl-tolyl-ketone.}}{\left.\begin{matrix}C_6H_5\\C_7H_7\end{matrix}\right\rangle CO} + M_2CO_3.$$

Interesting results have been reached through a study of the oximes of the aromatic ketones. It has been shown that while the symmetrical ketones, like benzophenone, $C_6H_5.CO.C_6H_5$, give but one oxime, some of the unsymmetrical ketones, like phenyl-tolyl-ketone, $C_6H_5.CO.C_6H_4.CH_3$, give two. This is quite in accordance with the views already set forth in regard to the stereochemistry of nitrogen compounds (see Benzaldoxime, page 314). In the terms of stereochemistry the two formulas

$$\begin{array}{c} C_6H_5.C.C_6H_5 \\ \| \\ HO.N \end{array} \qquad \text{and} \qquad \begin{array}{c} C_6H_5.C.C_6H_5 \\ \| \\ N.OH \end{array}$$

are identical, so that a symmetrical ketone can give but one oxime. On the other hand the formulas

$$\begin{array}{c} C_6H_5.C.C_6H_4.CH_3 \\ \| \\ HO.N \end{array} \qquad \text{and} \qquad \begin{array}{c} C_6H_5.C.C_6H_4.CH_3 \\ \| \\ N.OH \end{array}$$

are different, so that an unsymmetrical ketone can give two oximes.

Quinones.

The quinones are peculiar bodies which in some ways are allied to the ketones. The simplest example of the class, and the one best known, is called *quinone*. Its formula is $C_6H_4O_2$, and it therefore appears to be benzene in which two hydrogen atoms are replaced by two oxygen atoms. All quinones bear this relation to the hydrocarbons, of which they may be regarded as derivatives.

Quinone, $C_6H_4O_2$, is formed by the oxidation of quinic acid, hydroquinol, para-diamino-benzene, and some other benzene derivatives in which two substituting groups occupy the *para* position relatively to each other.

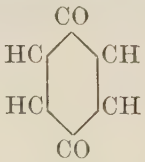
It is usually made by oxidizing aniline with sodium bichromate and sulphuric acid. In the laboratory it is most convenient to make it by oxidizing hydroquinol.

It forms long, yellow prisms; sublimes in golden-yellow needles; is volatile with steam; and has a peculiar penetrating odor.

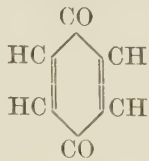
Sulphurous acid reduces quinone to hydroquinol: —

$$C_6H_4O_2 + 2\,HI = C_6H_4(OH)_2 + 2\,I.$$

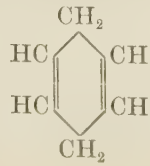
The easy transformation of hydroquinol into quinone, and the opposite transformation of quinone into hydroquinol, as well as the formation of quinone from other para compounds, force us to the conclusion that the oxygen atoms in quinone are in the para position relatively to each other. Quinone appears, therefore, as benzene containing two oxygen atoms in the para position as represented in the formula: —



As quinone forms a dioxime, and takes up four atoms of bromine and of chlorine, and two molecules of hydrochloric and of hydrobromic acid, most chemists regard it as a diketone of the formula: —

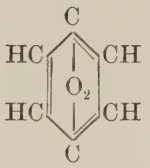


According to this view quinone is not, strictly speaking, a derivative of benzene, but is derived from dihydrobenzene: —



The easy changes from quinone to hydroquinol and from this back to quinone are not easily understood if this view is correct.

It has been suggested that quinone may be analogous to the peroxides, having its two oxygen atoms combined with each other thus: —



This represents quinone as a true derivative of benzene, and if it is analogous to the peroxides, it should be a strong oxidizing agent, as it is.

If the di-ketone formula is correct quinone may be regarded as derived from a dibasic acid in the same way that a simple ketone is derived from a monobasic acid. Thus, the calcium salt of an acid of the formula $C_2H_2 < \begin{matrix} COOH \\ COOH \end{matrix}$ ought, according to this view, to yield quinone by distillation: —

$$\left.\begin{matrix} C_2H_2 < \begin{matrix} CO \\ COO \end{matrix} > O > Ca \\ C_2H_2 < \begin{matrix} CO \\ COO \end{matrix} > O > Ca \end{matrix}\right\} = C_2H_2 < \begin{matrix} CO \\ CO \end{matrix} > C_2H_2 + 2\,CaCO_3.$$

Several quinones have been studied. Under the head of Anthracene we shall meet with an important one called *anthraquinone*, which has been made by reactions that prove it to be a di-ketone in the sense in which this expression is explained above.

Pyridine Bases, $C_nHN_{2n-5}N$.

The pyridine bases are formed in the distillation of bones, certain bituminous shales, and coal, and were first isolated from

bone oil, which is a complex mixture of many substances. At present these bases are obtained principally from coal tar. The principal members of the group are pyridine, picoline, lutidine, and collidine. They form an homologous series: —

Pyridine	C_5H_5N
Picoline	C_6H_7N
Lutidine	C_7H_9N
Collidine	$C_8H_{11}N$

The formation of these bases in the distillation of bones is due to the presence of acroleïn, ammonia, methylamine, etc., and their action upon one another at high temperatures. Members of the series are formed whenever aldehydes of the fatty series are heated with ammonia. For example, ordinary aldehyde and ammonia give methylethylpyridine, $C_8H_{11}N$, $C_5H_3(CH_3)(C_2H_5)N$: —

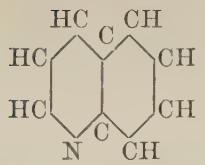
$$4\,C_2H_4O + NH_3 = C_8H_{11}N + 4\,H_2O;$$

and acroleïn and ammonia give β-picoline: —

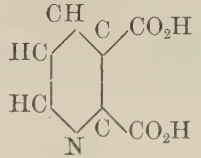
$$2\,C_3H_4O + NH_3 = C_6H_7N + 2\,H_2O.$$

Further, pyridine and picoline are formed when glycerol is distilled with ammonium sulphate and sulphuric acid.

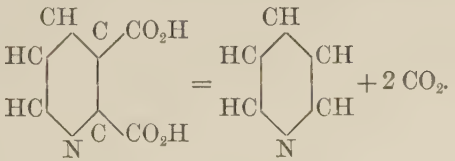
Pyridine, C_5H_5N. — Pyridine is found in commercial ammonia, and is formed, as stated above, in the distillation of bones, of certain bituminous shales, and of coal. It has been prepared from a number of its carboxyl derivatives, as, for example, from nicotinic acid, $C_5H_4N.CO_2H$, which is formed when nicotine is oxidized with nitric acid. The formation of pyridine from quinolinic acid, a dicarboxyl derivative of pyridine, is of special importance as it leads very clearly to a conception of the constitution of pyridine. Quinoline (which see) will be shown to have the constitution represented by the formula



When it is oxidized it gives the dibasic acid above referred to, quinolinic acid,



When this is distilled with lime it loses carbon dioxide and gives pyridine: —



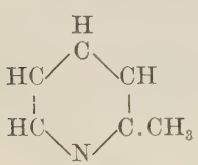
According to this, pyridine is benzene containing a nitrogen atom in place of one of the CH groups. The question in regard to the linkage of the groups and atoms in pyridine is a difficult one to deal with, and it need not be discussed here. Suffice it to say that the above hypothesis, as to the relation between benzene and pyridine, is in accordance with all the facts known.

Pyridine is a liquid with a peculiar, sharp characteristic odor. It boils at 116°. It acts like a monacid base, forming salts like $C_5H_5N \cdot HCl$, $C_5H_5N \cdot HNO_3$, $C_5H_5N \cdot H_2SO_4$, etc. It unites with alkyl iodides like methyl iodide, ethyl iodide, etc. When these compounds are treated with silver hydroxide, they form the corresponding hydroxides which are strong bases. The compounds with the alkyl iodides are converted by heat

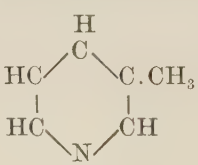
into salts of homologues of pyridine. For example, the ethyl iodide addition-product of pyridine is transformed at 290° into ethylpyridine hydriodide: —

$$C_5H_5N \,.\, C_2H_5I = C_2H_5 \,.\, C_5H_4N \,.\, HI.$$

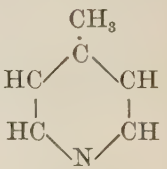
The view above presented has suggested various lines of investigation. Thus, if the above formula represents the relations between benzene and pyridine, it is clear that the existence of three isomeric mono-substitution products of pyridine ought to be possible. Thus, there should be three methyl-pyridines or picolines, three pyridine-carbonic acids, etc. The three picolines should correspond to the formulas



Ortho-picoline.



Meta-picoline.



Para-picoline.

All three picolines are known; and, by oxidation, they are converted into the three pyridine-carbonic acids, $C_5H_4N \,.\, CO_2H$; and these, when distilled with lime, yield pyridine and carbon dioxide.

Lutidines, $C_5H_3(CH_3)_2N$. — No less than six isomeric varieties of dimethylpyridine are possible according to the theory. Five of these have been prepared in pure condition. By oxidation they yield, first, monobasic acids, and then dibasic acids. When the monobasic acids are distilled with lime, they yield picolines. The dibasic acids give pyridine: —

$$NC_5H_3 < \begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow NC_5H_3 < \begin{matrix} CH_3 \\ CO_2H \end{matrix} \longrightarrow NC_5H_3 < \begin{matrix} CO_2H \\ CO_2H \end{matrix};$$

$$NC_5H_3 < \begin{matrix} CH_3 \\ CO_2H \end{matrix} = NC_5H_4 \,.\, CH_3 + CO_2;$$

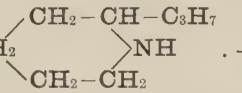
$$NC_5H_3 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = NC_5H_5 + 2\,CO_2.$$

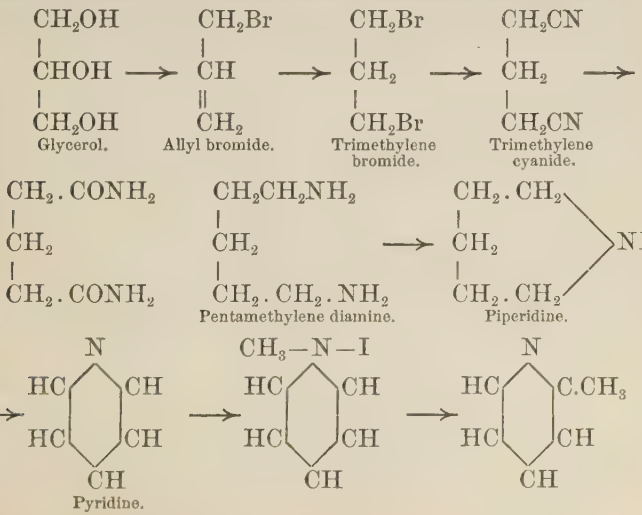
Conyrine, Propylpyridine, $NC_5H_4.C_3H_7$. — This base is formed when conine is heated with zinc chloride or when the hydrochloride of conine is heated with zinc dust. It is converted into picolinic acid by oxidation, and is reduced to conine by hydriodic acid.

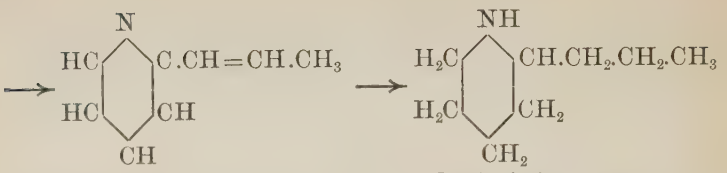
The pyridine bases unite with two, four, or six atoms of hydrogen. Some of the alkaloids are derivatives of the addition-products thus formed.

Piperidine, $C_5H_{11}N$. — This base is formed from piperine, a constituent of pepper. It has been made by adding hydrogen to pyridine by means of sodium and alcohol: —

$$C_5H_5N + 6\,H = C_5H_{11}N.$$

Conine, Propylpiperidine,  . — This base occurs together with others in hemlock (*Conium maculatum*). It is a colorless liquid, and is a violent poison. This is the first alkaloid that was prepared artificially, and it is therefore of special interest. The steps taken are indicated below: —





Inactive Conine.

The change from picoline to allyl-picoline is effected by means of paraldehyde. The conine thus obtained is optically inactive, whereas that obtained from hemlock is dextro-rotatory. By means of the salt with *d*-tartaric acid, the inactive conine can be resolved into the two active varieties. The *d*-conine thus obtained is identical with natural conine.

[Is there an asymmetric carbon atom in conine?]

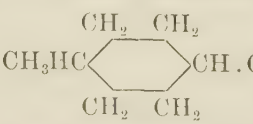
Terpenes.

Terpenes are hydrocarbons found in various coniferous trees. The volatile oil from these trees consists of hydrocarbons of the composition $C_{10}H_{16}$. The ethereal oils that are obtained by distilling fruits of many citrus varieties with water have the same composition. In some oils obtained from natural sources terpenes are found mixed with other substances, especially such as contain oxygen.

The terpenes can be classified into:—

(1) Terpenes, $C_{10}H_{16}$;
(2) Sesquiterpenes, $C_{15}H_{24}$;
(3) Diterpenes, $C_{20}H_{32}$;
(4) Polyterpenes, $(C_{10}H_{16})_x$.

All of these hydrocarbons are related to hexahydrocymene,



This is shown by the fact that many of the terpenes are

converted by gentle oxidation into cymene, and by oxidation with nitric acid into *p*-toluic and terephthalic acid.

Some of the terpenes take up one molecule of hydrochloric acid, others take up two molecules. They also combine with water and form hydrates. They are easily polymerized by heat or by shaking with sulphuric acid or with boron fluoride.

The terpenes proper of the formula, $C_{10}H_{16}$, may be conveniently divided into three groups: —

1. Olefin-terpene Group;
2. Terpane or Menthane Group;
3. Camphane Group.

1. Olefin-terpene Group.

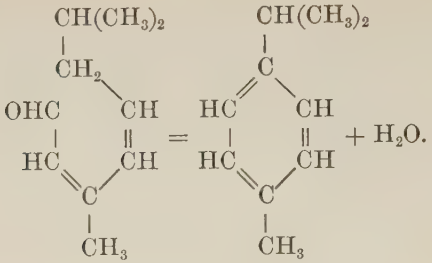
These compounds are not themselves derivatives of hydrocymene, but they are easily converted into such derivatives. They are unsaturated paraffins. The only ones that need be mentioned here are *isoprene*, C_5H_8, and *anhydrogeraniol*, $C_{10}H_{16}$. The former is an example of a *hemiterpene*. It is formed in the distillation of caoutchouc. It is probably *methyl-divinyl*,

Anhydrogeraniol is formed from geraniol, $C_{10}H_{18}O$, (which see) by elimination of water. It probably has the structure represented by the formula

$$(CH_3)_2C{=}CH\,.\,CH_2\,.\,CH_2\,.\,C(CH_3){=}C{=}CH_2.$$

As will be seen, it contains three double bonds. It has the power to take up six atoms of hydrogen or of bromine.

Geraniol, $C_{10}H_{18}O$, is contained in Indian oil of geranium and in a number of other ethereal oils. Its properties show clearly that it is a primary alcohol. By oxidation with chromic acid it gives an aldehyde, *geranial*, $C_{10}H_{16}O$, and an acid, *geranic acid*, $C_{10}H_{16}O_2$. Geranial loses water and gives cymene: —

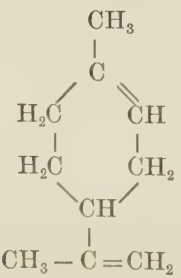


2. Terpane or Menthane Group.

The characteristic property of the members of this group is their power to take up four atoms of bromine or two molecules of hydrochloric or of hydrobromic acid.

Limonene, Dipentene, $C_{10}H_{16}$. — This is known in three varieties — dextro, levo, and inactive. The inactive variety occurs with cineol in *Oleum cinæ*, and is formed by heating pinene and camphene to 250–300°, and is therefore contained in Russian and Swedish oil of turpentine. *d*-Limonene is found in oil of citron, oil of bergamot, and a number of other ethereal oils. With bromine it forms a tetra-bromide, $C_{10}H_{16}Br_4$, that melts at 104–105°. *l*-Limonene is found in the oil of fir needles (*Pinus sylvestris*) and in oil of fir, together with *l*-pinene.

Limonene probably has the constitution represented by the formula



***l*-Menthol, $C_{10}H_{19}(OH)$,** is a solid, melting at 42° and boiling at 212°. It is the chief constituent of oil of peppermint. It is a hydroxyl derivative of hexa-hydrocymene, $C_{10}H_{20}$.

3. Camphene Group.

The two most important members of this group are pinene and camphene. Among the oxygen derivatives of camphene is camphor.

Pinene, $C_{10}H_{16}$. — This is the principal ingredient of the various kinds of oil of turpentine obtained from different varieties of pine. It also occurs in a number of ethereal oils. It combines with one molecule of hydrochloric or of hydrobromic acid; with two atoms of bromine; and with one molecule of water. When heated to 250–270° it is converted into an isomeric hydrocarbon dipentene (limonene). Pinene is known in three varieties: *dextro-*, *levo-*, and *inactive*. *d*-Pinene is obtained from American oil of turpentine; *l*-pinene from the French. The inactive variety is formed by combination of the two active varieties.

Pinene contains one double bond, as is shown by its union with one molecule of hydrobromic acid, and with two atoms of chlorine and of bromine. The constitution of pinene has not been definitely determined.

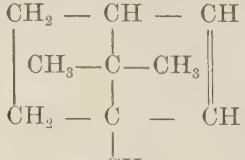
***d*-Pinene hydrochloride, $C_{10}H_{17}Cl$,** is formed by conducting dry hydrochloric acid gas into pinene. It is a crystalline solid with an odor like that of ordinary camphor. It is called *artificial camphor*. When heated alone, or with bases, hydrochloric acid is split off and a hydrocarbon isomeric with pinene is formed. This is *camphene*.

Oil of Turpentine. — When incisions are made in the trunk of various conifers, a liquid exudes which is known as *turpentine*. Most of that which comes into the market is obtained from *Pinus australis*, growing in North America. The volatile

constituent of turpentine is oil of turpentine. The other is *abietic acid*. These are separated by distillation. If the distillation is carried on without the addition of water, the residue is ordinary *rosin* (colophony).

Oil of turpentine dissolves sulphur, phosphorus, and caoutchouc, and is used in the preparation of varnishes and oil colors.

Camphene, $C_{10}H_{16}$. — This terpene is formed from borneol (which see) by heating it with acid potassium sulphate and by treating it with other reagents. There are several varieties of camphene known. It has already been stated that a camphene is formed by the elimination of hydrochloric acid from the hydrochloric acid addition-product of *l*-pentene. That which is thus obtained is known as *l*-camphene or *terecamphene*. Similarly a *d*-camphene is obtained from the pinene obtained from American oil of turpentine. Camphene has been shown to have the constitution represented by the formula, —



It is closely related to camphor, as will be pointed out.

Camphors.

Borneol, Borneo Camphor, $C_{10}H_{18}O$. — Borneo camphor is found in cavities in a tree (*Dryobalanops camphora*) that grows in Borneo, Sumatra, etc. This variety is dextro-rotatory. The levo-rotatory variety is found in the camphor from valerian oil, and inactive borneol is formed by bringing together *d*- and *l*-borneol. Borneol is much like ordinary camphor or laurinol, but its odor resembles that of pepper. When laurinol is treated with sodium and alcohol, it gives both *d*- and *l*-borneol: —

$$2\,C_{10}H_{16}O + 4\,H = C_{10}H_{18}O + C_{10}H_{18}O.$$
Laurinol. *d*-Borneol. *l*-Borneol.

Both of the active varieties are oxidized to laurinol by nitric acid. Borneol is an alcohol, as is shown by the action of phosphorus pentachloride and of glacial acetic acid. The former gives the chloride, $C_{10}H_{17}Cl$: —

$$C_{10}H_{17}(OH) + PCl_5 = C_{10}H_{17}Cl + POCl_3 + HCl.$$

The latter gives an acetate: —

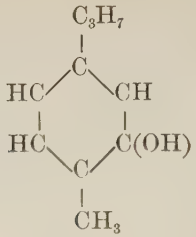
$$C_{10}H_{17}(OH) + HOOC\,.\,CH_3 = C_{10}H_{17}O\,.\,OC\,.\,CH_3 + H_2O.$$

Camphor, laurinol, $C_{10}H_{16}O$. — This is the substance ordinarily called *camphor*. It is obtained in China and Japan from different species of the genus *Camphora* of the *Laurus* family by distilling the finely cut wood with water vapor. It is purified by sublimation. It is a colorless mass that can be crystallized from alcohol and sublimes in lustrous prisms. The ordinary form is dextro-rotatory. Both the other possible stereo-isomeric forms are known. Camphor is reduced to borneol by hydrogen from sodium and alcohol. It can be made by oxidizing borneol or camphene. When distilled with phosphorus pentoxide, camphor gives cymene: —

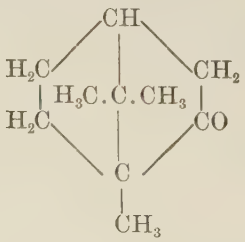
$$C_{10}H_{18}O = C_{10}H_{16} + H_2O.$$

The same decomposition is effected by heating camphor with concentrated hydrochloric acid to 170°.

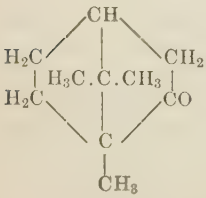
All the evidence goes to show that camphor is not an alcohol, but a ketone. The ease with which it is converted into cymene makes it highly probable that a methyl group and an isopropyl group are present in the compound in the para position in a benzene ring. It forms carvacrol by loss of two atoms of hydrogen. Carvacrol is isomeric with thymol, the hydroxyl being in the ortho position to the methyl group as shown in the formula, —



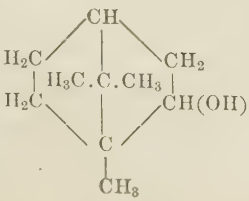
This makes it appear highly probable that the oxygen in camphor is ortho to methyl. Other facts that have been brought to light in investigations of the oxidation-products of camphor indicate that the group, $C(CH_3)_2$, formed from isopropyl is united with two para carbon atoms of the benzene ring. All this is shown by the formula for camphor now perhaps generally accepted by chemists: —



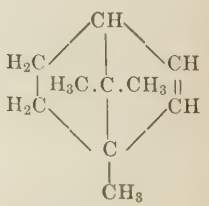
The relation between borneol, camphor, and camphene is shown by the formulas, —



Camphor.



Borneol.



Camphene.

CHAPTER XVI.

DI-PHENYL-METHANE, TRI-PHENYL-METHANE, TETRA-PHENYL-METHANE, AND THEIR DERIVATIVES.

As we have seen, toluene may be regarded either as methyl-benzene or phenyl-methane. Of course, according to all that is known regarding similar substances, the two views are identical. Regarding it, for our present purpose, as phenyl-methane, we may write its formula thus: $C\begin{cases} C_6H_5 \\ H \\ H \\ H \end{cases}$

This suggests the possibility of the existence of such substances as

Di-phenyl-methane . . . . . $C\begin{cases} C_6H_5 \\ C_6H_5 \\ H \\ H \end{cases}$,

Tri-phenyl-methane . . . . . $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ H \end{cases}$,

and *Tetra-phenyl-methane* . . . . . $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{cases}$.

All these hydrocarbons are known. The derivatives of tri-phenyl-methane are of special interest and importance.

There is one reaction by means of which these hydrocarbons

can be made very readily. It has also been used for the synthesis of many other hydrocarbons. It depends upon the remarkable fact that, when a hydrocarbon is brought together with a compound containing chlorine, and anhydrous aluminium chloride then added, hydrochloric acid is evolved, and union of the two substances is effected, the aluminium chloride not entering into the composition of the product. Thus, when benzene and benzyl chloride, $C_6H_5.CH_2Cl$, are brought together under ordinary circumstances, no action takes place; but, if some solid aluminium chloride is added, reaction takes place according to the following equation: —

$$C_6H_5.CH_2Cl + C_6H_6 = \underset{\text{Di-phenyl-methane.}}{C_6H_5.CH_2.C_6H_5} + HCl,$$

and di-phenyl-methane is formed.

Similarly, when chloroform and benzene are brought together in the presence of aluminium chloride, tri-phenyl-methane is formed according to this equation: —

$$CHCl_3 + 3\,C_6H_6 = \underset{\text{Tri-phenyl-methane.}}{CH(C_6H_5)_3} + 3\,HCl.$$

Another method by which these hydrocarbons can be made, consists in heating a chloride and a hydrocarbon together in the presence of zinc dust. Thus, benzyl chloride and benzene give di-phenyl-methane when boiled with zinc dust; and benzal chloride, $C_6H_5.CHCl_2$, and benzene give tri-phenyl-methane: —

$$C_6H_5.CHCl_2 + 2\,C_6H_6 = CH(C_6H_5)_3 + 2\,HCl.$$

Only tri-phenyl-methane will be treated of here.

Tri-phenyl-methane, $C_{19}H_{16}[= CH(C_6H_5)_3]$. — This hydrocarbon can be made, as above described, from benzal chloride and benzene, and from chloroform and benzene. It can also be made from benzal chloride and mercury diphenyl, $Hg(C_6H_5)_2$: —

$$C_6H_5.CHCl_2 + Hg(C_6H_5)_2 = CH(C_6H_5)_3 + HgCl_2.$$

It forms lustrous, thin laminæ, which melt at 92°. It is insoluble in water; easily soluble in ether and chloroform. It is crystallized best from alcohol.

Towards reagents it is very stable. Thus, ordinary concentrated sulphuric acid does not act upon it.

Oxidizing agents convert it into tri-phenyl-carbinol, $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ OH \end{cases}$.

That the oxidation-product is really tri-phenyl-carbinol appears probable, from the fact that whenever aromatic hydrocarbons that contain paraffin residues are oxidized, the paraffin residues are first attacked, while, as a rule, the benzene residue is unacted upon. Further, it gives an acetate with acetyl chloride; and with phosphorus pentachloride it gives a chloride which is decomposed by boiling water, giving the carbinol again. A bromide is formed by treating it with hydrobromic acid, and this gives the carbinol when boiled with water.

Trinitro-triphenyl-methane, $\}$ $C_{19}H_{13}(NO_2)_3[= CH(C_6H_4NO_2)_3]$, is formed by treating triphenyl-methane with nitric acid; and also by treating a mixture of nitro-benzene and chloroform with aluminium chloride: —

$$CHCl_3 + 3\,C_6H_5.NO_2 = CH(C_6H_4.NO_2)_3 + 3\,HCl.$$

This reaction shows that in the tri-nitro product one nitro group is contained in each benzene residue.

Triamino-triphenyl-methane, para-leucaniline, $C_{19}H_{13}(NH_2)_3[= CH(C_6H_4.NH_2)_3]$.

The tri-amino compound is made by reduction of the tri-nitro compound, and also by reduction of para-rosaniline. It is converted into para-rosaniline by oxidation.

Triphenyl-methane Dyes.

The well-known substances included under the head of Triphenyl-methane Dyes are more or less simple derivatives of the two compounds called *rosaniline* and *para-rosaniline*.

When mixtures of aniline and the toluidines are heated together with different oxidizing agents, such as arsenic acid, stannic chloride, mercuric chloride, etc., several substances are formed, the principal of which are the two above named. Para-rosaniline, $C_{19}H_{19}N_3O$, is formed from para-toluidine and aniline, according to the equation, —

$$\underset{\text{Aniline.}}{2\,C_6H_7N} + \underset{\text{}p\text{-Toluidine.}}{C_7H_9N} + 3\,O = \underset{\text{Para-rosaniline.}}{C_{19}H_{19}N_3O} + 2\,H_2O.$$

Rosaniline, $C_{20}H_{21}N_3O$, is formed in a similar way: —

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{}o\text{- and }p\text{-Toluidines.}}{2\,C_7H_9N} + 3\,O = \underset{\text{Rosaniline.}}{C_{20}H_{21}N_3O} + 2\,H_2O.$$

The composition and modes of formation of the two substances show that rosaniline is a homologue of para-rosaniline, the relation between the two substances being represented by the formulas $C_{19}H_{19}N_3O$ and $C_{19}H_{18}(CH_3)N_3O$.

By treating para-rosaniline with a reducing agent, it is converted into para-leucaniline, which has been shown to be triamino-triphenyl-methane: —

$$\underset{\text{Para-rosaniline.}}{C_{19}H_{19}N_3O} + H_2 = \underset{\text{Para-leucaniline.}}{C_{19}H_{19}N_3}\left\{ = C\left\{\begin{matrix} C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \\ H \end{matrix}\right.\right. + H_2O.$$

It will thus be seen that para-rosaniline and rosaniline, which are the fundamental compounds of the group of aniline dyes, are derivatives of the hydrocarbon tri-phenyl-methane.

Para-rosaniline, $C_{19}H_{19}N_3O$. — The formation of this substance by oxidation of para-leucaniline and of a mixture of toluidine and aniline was mentioned above. The relation between para-rosaniline and para-leucaniline is probably expressed by the following formulas: —

$$\underset{\text{Tri-phenyl-methane.}}{CH\left\{\begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\right.} \qquad \underset{\text{Triamino-triphenyl-methane, or Para-leucaniline.}}{CH\left\{\begin{matrix} C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \end{matrix}\right.} \qquad \underset{\text{Triamino-triphenyl-carbinol, or Para-rosaniline.}}{C(OH)\left\{\begin{matrix} C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \\ C_6H_4\,.\,NH_2 \end{matrix}\right.}$$

Rosaniline, $C_{20}H_{21}N_3O$. — This is the principal constituent of commercial fuchsine. It is formed by oxidizing a mixture of aniline and ortho- and para-toluidines: —

$$C_6H_7N + 2\,C_7H_9N + 3\,O = C_{20}H_{21}N_3O + 2\,H_2O.$$

Experiment 77. In a dry test-tube put a little dry mercuric chloride and a few drops of commercial aniline. Heat over a small flame. Dissolve the product in alcohol, with the addition of a little hydrochloric or acetic acid. The beautiful color of the solution is due to the presence of the hydrochloride or acetate of rosaniline.

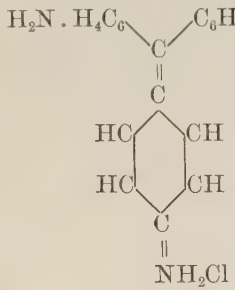
On the large scale, the oxidizing agent used is arsenic acid. Care is taken to remove all arsenic acid from the product, but it is nevertheless sometimes found in the products obtained in the market. Nitro-benzene is also used as the oxidizing agent. In this case there is, of course, no arsenic in the product. Rosaniline crystallizes in needles or plates. It is very slightly soluble in water; more readily soluble in alcohol. It forms three series of salts with monobasic acids. With hydrochloric acid it forms the salts $C_{20}H_{19}N_3 . HCl$ and $C_{20}H_{19}N_3 . 3\,HCl$. The former is the substance known as *fuchsine*, though some of the fuchsine met with in the market is the acetate of rosaniline, $C_{20}H_{19}N_3 . C_2H_4O_2$. The formation of the salts of para-rosaniline takes place as represented in the following equation: —

$$\underset{\text{Para-rosaniline.}}{C(OH)(C_6H_4 . NH_2)_3} + HCl = \underset{\text{Para-rosaniline hydrochloride.}}{C\begin{cases} C_6H_4 . NH_2 \\ C_6H_4 . NH_2 . \\ C_6H_4 . NH . HCl \end{cases}}$$

Instead of the formulas here given for the salt two others have been suggested. In one of these the salt is represented as derived from the base triamino-triphenyl-carbinol or para-rosaniline as potassium chloride is formed from potassium hydroxide: —

$$\left.\begin{matrix} NH_2 . C_6H_4 \\ NH_2 . C_6H_4 \\ NH_2 . C_6H_4 \end{matrix}\right\} C(OH) \qquad \left.\begin{matrix} NH_2 . C_6H_4 \\ NH_2 . C_6H_4 \\ NH_2 . C_6H_4 \end{matrix}\right\} CCl.$$

According to the other view the salt and all the colored salts derived from para-rosaniline and similar bases have a constitution similar to that of quinone as shown thus for the hydrochloric acid salt of para-rosaniline: —



or $(C_6H_4NH_2)_2C = C_6H_4 = NH_2Cl$.

Fuchsine and the other salts of rosaniline dye wool and silk directly. For dyeing cotton cloth, however, a *mordant* is generally necessary.

Dyeing. Animal fibres, in general, are colored directly by dyes; that is to say, they have the power of forming with the dyes stable compounds which adhere to the fibres. This is not generally true of vegetable fibres, as cotton cloth and linen. Hence, in order to dye the latter, something must be added that, with the dye, forms a compound which adheres to the fibres. Substances which act in this way are called *mordants*. Among the substances used as mordants are aluminium acetate, ferric acetate, and some salts of tin.

Experiment 78. Make a dilute solution of picric acid by dissolving 2g to 3g in 200cc to 300cc water. In a portion of it suspend a few pieces of white yarn or flannel. The *woollen* material will be strongly dyed yellow. In another portion suspend a piece of ordinary cotton cloth.

It should be noted that some dyes are applicable to cotton without mordants. These are called *substantive dyes*.

Acid fuchsine is a sulphonic acid of rosaniline. It is formed by treating rosaniline with concentrated sulphuric acid at 120°. It is soluble in water, and is a valuable dye.

Aniline dyes. — By introducing various hydrocarbon residues into para-rosaniline or rosaniline, in place of some or all of the hydrogen atoms of the amino groups, dyes of other colors are formed. The general effect of introducing methyl groups is to form dyes of a violet color. As the number of methyl groups increases, the product has a deeper blue tint.

Hexamethyl-para-rosaniline. — The hydrochloric acid salt of this is the well-crystallized dye, *crystal violet*, $[C_6H_4 . N(CH_3)_2]_2C : C_6H_4 : N(CH_3)_2Cl$. It is one of the principal constituents of *methyl* violet. Some of the methods used in preparing this dye are of special interest. It is made: —

(1) By the action of para-tetra-methyl-diamino-benzophenone on dimethyl-aniline in the presence of dehydrating agents: —

$$\left.\begin{matrix}(CH_3)_2N . C_6H_4 \\ (CH_3)_2N . C_6H_4\end{matrix}\right\rangle CO + C_6H_5 . N(CH_3)_2HCl =$$
$$C_{19}H_{12}N_3(CH_3)_6Cl + H_2O.$$

(2) By heating dimethyl-aniline with carbonyl chloride and aluminium chloride or zinc chloride: —

$$COCl_2 + 2\ C_6H_5 . N(CH_3)_2 = CO \left\langle \begin{matrix}C_6H_4 . N(CH_3)_2 \\ C_6H_4 . N(CH_3)_2\end{matrix}\right. + 2\ HCl;$$
$$CO \left\langle \begin{matrix}C_6H_4 . N(CH_3)_2 \\ C_6H_4 . N(CH_3)_2\end{matrix}\right. + C_6H_5 . N(CH_3)_2HCl =$$
$$C_{19}H_{12}N_3(CH_3)_6Cl + H_2O.$$

Methyl violet consists of crystal violet mixed with products containing a smaller number of methyl groups.

Methyl green is an addition product formed by the action of methyl chloride on an alcoholic solution of methyl violet.

Hofmann's violet (*Dahlia*) is either the hydrochloric acid or acetic acid salt of tri-methyl-rosaniline. It is made by heating together a salt of rosaniline, methyl iodide, and methyl alcohol.

Aniline blue is the hydrochloride of tri-phenyl-rosaniline. It is formed by heating salts of rosaniline with aniline and some benzoic acid.

Soluble blue is a sulphonic acid of aniline blue.

Phthaleïns.

In speaking of phthalic anhydride, it was stated that when this substance is treated with phenols, phthaleïns are formed; and, in speaking of resorcinol, a markedly fluorescent body was mentioned as being formed when phthalic acid and resorcinol are heated together.

Phenol-phthaleïn, $C_{20}H_{14}O_4$. — This substance is formed by heating a mixture of phenol and phthalic anhydride with sulphuric acid or some other dehydrating agent: —

$$\underset{\text{Phenol.}}{2\,C_6H_6O} + \underset{\text{Phthalic anhydride.}}{C_8H_4O_3} = \underset{\text{Phenol-phthaleïn.}}{C_{20}H_{14}O_4} + H_2O.$$

The fused mass is dissolved in caustic soda, and the phenol-phthaleïn precipitated by the addition of an acid. It forms a granular crystalline powder. Its solution in alkalies is red or violet, according to the thickness of the layer. Acids destroy the color. Hence it may be used as an indicator in alkalimetry as a substitute for litmus.

Phenol-phthaleïn, like rosaniline, is a derivative of tri-phenyl-methane, as has been shown by the following somewhat complicated reactions: —

The chloride of phthalic acid, or phthalyl chloride, $C_8H_4O_2Cl_2$, when treated with benzene in the presence of aluminium chloride, gives up its two atoms of chlorine, and in their place takes up two phenyl groups, thus: —

$$\underset{\text{Phthalyl chloride.}}{C_8H_4O_2Cl_2} + 2\,C_6H_6 = \underset{\text{Diphenyl-phthalide.}}{C_8H_4O_2(C_6H_5)_2} + 2\,HCl.$$

The substance thus formed is known as *diphenyl-phthalide*. Its conduct towards water and bases is such as to show that it is the anhydride of an acid: —

$$C_8H_4O_2(C_6H_5)_2 + H_2O = C_8H_6O_3(C_6H_5)_2$$

$$\text{or } C_7H_5O\begin{cases} CO_2H \\ (C_6H_5)_2 \end{cases}.$$

When this acid is reduced by means of zinc dust it loses oxygen: —

$$C_7H_5O\begin{cases}CO_2H\\(C_6H_5)_2\end{cases} = C_7H_5\begin{cases}CO_2H\\(C_6H_5)_2\end{cases} + O.$$

And, finally, when the last product is distilled with baryta, it loses carbon dioxide and yields tri-phenyl-methane: —

$$C_7H_5\begin{cases}CO_2H\\(C_6H_5)_2\end{cases} = CH\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\end{cases} + CO_2.$$

We have thus passed from phthalic anhydride to triphenyl-methane, and the reactions just referred to are in all probability correctly represented by the following formulas and equations: —

$$C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO\\O\text{——}\end{cases} + H_2O = C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO_2H.\\OH\end{cases}$$

Diphenyl-phthalide, or anhydride of triphenyl-carbinol-carbonic acid.

Triphenyl-carbinol-carbonic acid.

$$C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\OH\end{cases} = C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\H\end{cases} + O.$$

Triphenyl-methane-carbonic acid.

$$C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\H\end{cases} = C\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\\H\end{cases} + CO_2.$$

Triphenyl-methane.

Now, by making dinitro-diphenyl-phthalide, reducing it, and boiling the diazo compound with water, the product is phenol-phthaleïn. Hence, the latter compound appears to be the dihydroxy derivative of diphenyl-phthalide: —

$$C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases} \qquad C\begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases} \qquad C\begin{cases} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases}.$$

Phenol-phthaleïn.

The formula for phenol-phthaleïn may also be written thus: —

$$\begin{matrix} C_6H_4.OH \\ C_6H_4.OH \end{matrix} > C < \begin{matrix} C_6H_4 \\ O \end{matrix} > CO,$$

the curious arrangement of the carbonyl group being simply the sign of the anhydride condition between carboxyl and hydroxyl, of which the simplest expression is

$$R < \begin{matrix} OH \\ COOH \end{matrix} = R < \begin{matrix} O \\ | \\ CO \end{matrix} + H_2O.$$

This plainly is the characteristic grouping of the lactones (see page 166).

There is reason to believe that when a phthaleïn is treated with a base and converted into a salt the constitution is essentially changed, the resulting salt having a quinone-like structure as shown thus: —

$$C\begin{cases} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases} \qquad C\begin{cases} C_6H_4.OH \\ =C_6H_4=O \\ C_6H_4.COOK \end{cases} \qquad \text{or}$$

Free phenol-phthaleïn (lactoid formula).

$$O=C_6H_4=C<\begin{matrix} C_6H_4.OH \\ C_6H_4.COOK \end{matrix}$$

Salt of phenol-phthaleïn (quinoid-formula).

Note for Student. — Although the reactions above briefly described may at first sight appear to be difficult to comprehend, they are in reality simple enough. The student is earnestly recommended not to slight them on account of the long names and complex formulas involved. They afford

an excellent example of the methods upon which we rely for determining the nature of complex substances. Notice that all appears dark until the well-known substance tri-phenyl-methane is obtained, which suggests that all the substances are derivatives of this fundamental hydrocarbon; and how easily, when this conception has once been formed, the interpretation of all the reactions follows.

Among the other phthaleïns that deserve special mention is that which is formed with resorcinol.

Fluoresceïn, resorcinol-phthaleïn, $C_{20}H_{12}O_5$. — This beautiful substance is formed by heating together resorcinol and phthalic anhydride to 200° : —

$$2\,C_6H_4(OH)_2 + C_8H_4O_3 = C_{20}H_{12}O_5 + 2\,H_2O.$$

Its solutions in alkalies are wonderfully fluorescent. The substance, which is sold under the name "*uranin*" for the purpose of exhibiting the phenomenon of fluorescence, is an alkaline salt of fluoresceïn.

From the solutions of its salts fluoresceïn is precipitated as a yellow powder of the composition, $C_{20}H_{14}O_6$. This loses water readily on standing, and forms the compound, $C_{20}H_{12}O_5$, which is yellowish red. The fact that the compound is colored has led to the belief that it has the quinoid structure in the free conditions as well as in its salts.

The reaction that takes place between resorcinol and phthalic anhydride, when fluoresceïn is formed, is of the same kind as that which takes place between phenol and the anhydride to form phenol-phthaleïn. We should therefore expect to find that fluoresceïn has the formula : —

$$C\begin{cases} C_6H_3\begin{cases} OH \\ OH \end{cases} \\ C_6H_3\begin{cases} OH \\ OH \end{cases} \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases} \quad \text{or} \quad C\begin{cases} C_6H_4{<}\begin{matrix} OH \\ OH \end{matrix} \\ =C_6H_3{=}O \\ C_6H_4COOH \end{cases}$$

which shows its analogy to phenol-phthaleïn,

$$C\begin{cases} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases}$$

It is found, however, that in reality fluoresceïn corresponds to the above formula less one molecule of water; and it is believed that the water is given off as represented thus: —

$$C\begin{cases} C_6H_3\begin{cases} OH \\ O \\ OH \end{cases} \\ C_6H_3 \\ C_6H_4.CO \\ O\text{——}\rfloor \end{cases} \quad \text{or} \quad C\begin{cases} C_6H_3<\begin{matrix} OH \\ O \end{matrix} \\ \diagup \\ =C_6H_3=O \\ C_6H_4.COOH \end{cases}$$

Fluoresceïn.

Eosin, tetra-brom-fluoresceïn, $C_{20}H_8Br_4O_5$, is formed by treating fluoresceïn with bromine. Its dilute solutions have an exquisite, delicate pink color which suggests a color often seen in the sky at the dawn of day. Hence the name *eosin*, from ἠώς, *dawn*. It is fluorescent, and is used as a dye.

CHAPTER XVII.

HYDROCARBONS, C_nH_{2n-8}, AND DERIVATIVES.

The hydrocarbons thus far considered are of three classes. They are: (1) paraffins, or saturated hydrocarbons of the marsh-gas series; (2) unsaturated hydrocarbons related to the paraffins; and (3) hydrocarbons which contain residues of the saturated paraffins and of benzene.

We now pass to a brief consideration of a hydrocarbon which is made up of a residue of benzene and of an unsaturated paraffin. It bears to ethylene the same relation that toluene bears to marsh gas; that is to say, it is phenyl-ethylene.

Styrene, phenyl-ethylene, $C_8H_8(C_6H_5 . CH . CH_2)$. — This hydrocarbon is contained in liquid storax, — a fragrant, honey-like substance which exudes from various plants, as the liquid-amber and in coal-tar xylenes. It is formed by distilling cinnamic acid with lime: —

$$C_9H_8O_2 = C_8H_8 + CO_2.$$

Note for Student. — What does this reaction suggest with regard to the relation between cinnamic acid and styrene?

It is also formed from phenyl-ethane, $C_6H_5.C_2H_5$, in the same way that ethylene is formed from ethane: —

$$\left\{\begin{array}{lll} C_2H_6 + Br_2 = C_2H_5Br + HBr \\ C_2H_5Br + KOH = C_2H_4 + KBr + H_2O \end{array}\right.;$$

$$\begin{array}{lll} C_6H_5.C_2H_5 + Br_2 = C_6H_5.C_2H_4Br + HBr; \\ C_6H_5.C_2H_4Br + KOH = C_6H_5.C_2H_3 + KBr + H_2O. \end{array}$$

Styrene.

Its formation by heating acetylene was mentioned on p. 242: —

$$4\,C_2H_2 = C_8H_8.$$

NOTE FOR STUDENT. — What other polymeric product is obtained by heating acetylene?

Styrene is a liquid of an aromatic odor; boils at 140°; insoluble in water; miscible with ether and alcohol in all proportions.

When heated alone up to 300°, or even when allowed to stand at ordinary temperatures, it is converted into a polymeric modification called *meta-styrene*, which is a solid. This same change is readily effected by several reagents, such as iodine and concentrated sulphuric acid. Styrene unites directly with chlorine and bromine in the same way that ethylene does (see p. 227): —

$$C_6H_5 . CH : CH_2 + 2\,Br = C_6H_5 . CHBr . CH_2Br.$$

It unites with hydrobromic acid, forming phenyl-ethyl bromide: —

$$C_6H_5 . CH : CH_2 + HBr = C_6H_5 . CH_2 . CH_2Br.$$

Hydriodic acid reduces it to phenyl-ethane: —

$$C_6H_5 . CH : CH_2 + 2\,HI = C_6H_5 . CH_2 . CH_3 + 2\,I.$$

Chromic acid and other oxidizing agents convert styrene into benzoic acid (see remarks, p. 265). Some higher members of this series have been prepared, such as *phenyl-propylene*, *phenyl-butylene*, etc.; but at present they are not of sufficient importance to make their consideration necessary.

Styrene is closely related to cinnamic acid, from which the interesting and important compounds of the indigo group are obtained.

Styryl alcohol, $C_9H_{10}O(C_6H_5 . CH : CH . CH_2OH)$. — This alcohol occurs in nature in the form of an ethereal salt of cinnamic acid in liquid storax, and also in balsam of Peru. It forms long, thin needles, which melt at 33°. It boils

at 250°. It takes up hydrogen, and yields phenyl-propyl alcohol, $C_6H_5 . CH_2 . CH_2 . CH_2OH$ (see p. 312): —

$$C_6H_5 . CH : CH . CH_2OH + H_2 = C_6H_5 . CH_2 . CH_2 . CH_2OH.$$

By treatment with hydriodic acid it yields allyl-benzene (phenyl-propylene), $C_6H_5 . CH : CH . CH_3$, and toluene.

When oxidized with platinum black it is converted into the corresponding aldehyde, cinnamic aldehyde; and, by further oxidation, into cinnamic acid. The relations between the three substances are the familiar ones of a primary alcohol, and the corresponding aldehyde and acid: —

$C_6H_5 . CH : CH . CH_2OH$. Styryl alcohol. $\qquad$ $C_6H_5 . CH : CH . CHO$. Cinnamic aldehyde.

$C_6H_5 . CH : CH . CO_2H$. Cinnamic acid.

These compounds are the β-phenyl derivatives of allyl alcohol, acroleïn, and acrylic acid: —

$CH_2 : CH . CH_2OH$. Allyl alcohol. $\qquad$ $CH_2 : CH . CHO$. Acroleïn or acrylic aldehyde. $\qquad$ $CH_2 : CH . CO_2H$. Acrylic acid.

Cinnamic acid, Phenyl-acrylic acid, } $C_9H_8O_2 (C_6H_5 . CH : CH . CO_2H)$.

Cinnamic acid is found in liquid storax, partly in the free condition, and partly in the form of an ethereal salt in combination with styryl alcohol, as styryl cinnamate, in the balsams of Tolu and Peru. It can be made synthetically: —

1. By heating together benzoic aldehyde and acetyl chloride: —

$$C_6H_5 . COH + CH_3 . COCl = C_6H_5 . C_2H_2 . CO_2H + HCl.$$

This reaction will be better understood by writing it in two equations: —

(1) $C_6H_5 . CH\boxed{O} + C\boxed{H_2}H . COCl = C_6H_5 . CH : CH . COCl + H_2O$; Cinnamyl chloride.

(2) $C_6H_5 . CH : CH . COCl + H_2O = C_6H_5 . CH : CH . CO_2H + HCl$. Cinnamyl chloride.

The kind of action represented in equation (1) is not uncommon. We have already met with it in the formation of mesitylene from acetone (see p. 265), in which case two hydrogens from each of three methyl groups unite with an oxygen atom from each of the three carbonyl groups. The product is called a *condensation-product*, and the action is known as condensation. It has already been referred to under the head of *aldol condensation* (see p. 188).

2. By heating together benzoic aldehyde, sodium acetate, and acetic anhydride. The first reaction is that of addition: —

$$C_6H_5.\overset{H}{C}=O + HCH_2.CO_2Na = C_6H_5-\overset{H}{\underset{\underset{CH_2\cdot CO_2Na}{|}}{C}}-OH.$$

The acetic anhydride acts as a dehydrating agent and converts the product first formed into sodium cinnamate: —

$$C_6H_5.\overset{H}{\underset{\underset{CH_2.CO_2Na}{|}}{C}}-OH = C_6H_5.CH:CH.CO_2Na + H_2O.$$

3. By treating benzal chloride with sodium acetate: —

$$C_6H_5.CH\boxed{Cl_2}+C\boxed{H_2}H.CO_2Na = C_6H_5.CH:CH.CO_2Na+2HCl.$$

$$C_6H_5.CH:CH.CO_2Na + HCl = C_6H_5.CH:CH.CO_2H + NaCl.$$

The acid is now manufactured on the large scale by the last method.

Cinnamic acid is a solid which crystallizes in monoclinic prisms. It melts at 133°, and boils at 300° to 304°. It is easily decomposed into styrene and carbon dioxide: —

$$C_6H_5.CH:CH.CO_2H = C_6H_5.CH:CH_2 + CO_2.$$

Oxidizing agents convert it first into benzoic aldehyde and then into benzoic acid. Nascent hydrogen converts it into hydro-cinnamic or phenyl-propionic acid, $C_6H_5.CH_2.CH_2.CO_2H$ (p. 326). It unites with hydrochloric, hydrobromic, and hydriodic acids: —

$$C_6H_5 . C_2H_2 . CO_2H + HCl = C_6H_5 . C_2H_2Cl . CO_2H.$$
Phenyl-chlor-propionic acid.

Bromine yields the addition-product $C_6H_5 . C_2H_2Br_2 . CO_2H$. Treated with substituting agents, such as nitric acid, etc., it yields substitution-products in which the entering atoms or groups are contained in the benzene residue, in the ortho and para positions relatively to the acrylic acid residue, $C_2H_2 . CO_2H$.

Nitro-cinnamic acids, $C_6H_4\begin{cases} C_2H_2 . CO_2H \\ NO_2 \end{cases}$. — The ortho- and para-acids are formed by dissolving cinnamic acid in nitric acid.

Note for Student. — What are the products when toluene is treated with nitric acid? When benzoic acid is treated in the same way? To which case is the above analogous?

Amino-cinnamic acids, $C_6H_4\begin{cases} C_2H_2 . CO_2H \\ NH_2 \end{cases}$. — These acids are formed by treating the nitro-acids with reducing agents. The ortho-acid loses water when set free from its salts, and forms the anhydride *carbostyril*, $C_6H_4\begin{cases} CH=CH \\ \quad | \\ NH-CO \end{cases}$ or $C_6H_4\begin{cases} CH=CH \\ \quad | \\ N=C(OH) \end{cases}$, analogous to hydro-carbostyril (p. 326).

Coumarin, $C_9H_6O_2\left(C_6H_4\begin{cases} C_2H_2CO \\ O— \end{cases}\right)$, is a compound found in Tonka beans, and in many other plant substances. It is made synthetically from salicylic aldehyde, sodium acetate, and acetic anhydride, just as cinnamic acid is made from benzoic aldehyde, sodium acetate, and acetic anhydride. The first product of this action is probably *ortho-hydroxy-cinnamic acid*, or coumaric acid, $C_6H_4\begin{cases} C_2H_2 . COOH \\ OH_{(o)} \end{cases}$, which then loses water, yielding the anhydride or coumarin. Coumarin has a pleasant odor, like that of sweet clover, and is used in perfumery. In very great dilution it has the odor of *new-mown hay*. Treated with bases, it yields salts of coumaric acid.

CHAPTER XVIII.

PHENYL-ACETYLENE AND DERIVATIVES.

Phenyl-acetylene, acetenyl-benzene, $C_6H_5 . C : CH$, bears to acetylene the same relation that styrene, or phenyl-ethylene, bears to ethylene. It is made from styrene in the same way that acetylene is made from ethylene: —

(1) $C_2H_4 + Br_2 = C_2H_4Br_2$;

(2) $C_2H_4Br_2 + 2\,KOH = C_2H_2 + 2\,KBr + 2\,H_2O$.

$C_6H_5 . C_2H_3 + Br_2 = C_6H_5 . C_2H_3Br_2$;

$C_6H_5 . C_2H_3Br_2 + 2\,KOH = C_6H_5 . C_2H + 2\,KBr + 2\,H_2O$.
Phenyl-acetylene.

It is a liquid that boils at 139° to 140°. It unites directly with four atoms of bromine, forms metallic derivatives, and, in general, conducts itself like acetylene (which see).

Phenyl-propiolic acid, $C_9H_6O_2 (= C_6H_5 . C : C . CO_2H)$. — This acid is a carboxyl derivative of phenyl-acetylene, bearing to it the same relation that cinnamic acid bears to phenyl-ethylene. It is made from cinnamic acid, by treating the dibromine addition-product with alcoholic potash. The reaction takes place in two stages: —

$$C_6H_5 . CHBr . CHBr . CO_2H = C_6H_5 . CH : CBr . CO_2H + HBr;$$

$$C_6H_5 . CH : CBr . CO_2H = C_6H_5 . C : C . CO_2H + HBr.$$

It forms long needles, which melt at 136° to 137°. When heated with water 120°, it breaks up into carbon dioxide and phenyl-acetylene.

Ortho-nitro-phenyl-propiolic acid, $C_6H_4 \begin{cases} C_2 . CO_2H \\ NO_{2(o)} \end{cases}$, is made from the dibromide of ortho-nitro-cinnamic acid, in the same way that phenyl-propiolic acid is made from the dibromide

of cinnamic acid (see preceding paragraph). It is of special interest, for the reason that it can easily be transformed into indigo. The transformation is most readily effected by boiling it with alkalies and grape sugar, or some other mild reducing-agent. The reaction is represented by the following equation: —

$$2\,C_6H_4\begin{cases}C_2\cdot CO_2H\\NO_{2(o)}\end{cases}+H_4=\underset{\text{Indigo.}}{C_{16}H_{10}N_2O_2}+2\,CO_2+2\,H_2O.$$

Ortho-nitro-phenyl-propiolic acid.

Indigo and Allied Compounds.

In several plants, *Indigofera tinctoria*, *Isatis tinctoria*, etc., there occurs a glucoside called *indican*, which, under the influence of dilute mineral acids and certain ferments, breaks up, yielding indigo-blue and a substance belonging to the glucose group. The indigo of commerce is prepared in the East and West Indies, in South America, Egypt, and other warm countries. At the proper stage the plants are cut off down to the ground, put in a large tank, and covered with water. Fermentation takes place, the indican breaking up and yielding indigo, as above stated. The liquid becomes green, and then blue. When the fermentation is finished, the liquid is drawn off into a second tank. This liquid contains the coloring-matter in solution. In contact with the air it is oxidized, forming indigo, which, being insoluble, is thrown down. In order to facilitate the precipitation of the indigo, the liquid is thoroughly stirred. Finally, the liquid is drawn off, the precipitated indigo pressed and dried, and then sent into the market.

The substance prepared as above has a dark-blue color, and contains other coloring-matters besides indigo-blue. Its value depends upon the amount of the definite compound, indigo-blue, contained in it.

Indigo-blue, indigotin, $C_{16}H_{10}N_2O_2$. — Indigo-blue is obtained from commercial indigo by reducing it to indigo-white,

and then exposing the clear colorless solution to the air, when indigo-blue is precipitated.

Experiment 79. Into a test-tube put a small quantity of powdered indigo; add fine zinc filings or zinc dust and caustic soda. When the mixture is heated the indigo forms a colorless solution. When this result has been reached, pour some of the solution into a small evaporating-dish. Contact with the air colors it blue.

Indigo-blue can be made artificially by a number of methods, among which the two following are the principal ones: —

1. By boiling ortho-nitro-phenyl-propiolic acid (which see) with an alkali and grape sugar.

2. From ortho-amino-benzoic (anthranilic) acid by treating it with chlor-acetic acid and fusing the product thus obtained with caustic potash: —

(1) $C_6H_4 < \begin{matrix} NH_2 \\ CO_2H \end{matrix} + ClCH_2 . CO_2H = C_6H_4 < \begin{matrix} NH . CH_2 . CO_2H \\ COOH \end{matrix} + HCl;$

(2) $C_6H_4 < \begin{matrix} NH . CH_2 . COOH \\ COOH \end{matrix} = C_6H_4 < \begin{matrix} NH \\ CO \end{matrix} > CH . COOH + H_2O;$

(3) $2\, C_6H_4 < \begin{matrix} NH \\ CO \end{matrix} > CH . COOH = C_6H_4 < \begin{matrix} NH \\ CO \end{matrix} > C : C < \begin{matrix} NH \\ CO \end{matrix} > C_6H_4 + 2\, CO_2 + 2\, H_2.$

The later method is now used on the large scale very successfully. The anthranilic acid is prepared from phthalic acid, which is prepared from naphthalene by oxidizing it with concentrated sulphuric acid in the presence of a little mercury. The history of the attempts to prepare indigo synthetically is full of interest. At present the artificially prepared product is driving natural indigo out of the market.

Indigo-blue crystallizes from aniline in dark-blue crystals. It sublimes in rhombic crystals. Its vapor has a purple-red color. It is insoluble in water, alcohol, and ether; soluble in

aniline and chloroform. Oxidizing agents convert it into isatine (which see). Heated with solid caustic potash, it yields carbon dioxide and aniline; boiled with a solution of caustic potash and finely-powdered black oxide of manganese, it is converted into ortho-amino-benzoic acid (anthranilic acid) (see p. 321).

Indigo-white, $C_{16}H_{12}N_2O_2$, is formed by reduction of indigo-blue, as above described. Its solutions rapidly turn blue in the air, in consequence of the formation of indigo-blue.

When indigo is oxidized with nitric acid, isatine, $C_8H_5NO_2$, is formed: —

$$C_{16}H_{10}N_2O_2 + O_2 = 2\ C_8H_5NO_2.$$

When isatine is treated with sodium amalgam, it takes up hydrogen, and yields *dioxindol*, $C_8H_7NO_2$: —

$$\underset{\text{Isatine.}}{C_8H_5NO_2} + H_2 = \underset{\text{Dioxindol.}}{C_8H_7NO_2}.$$

By further reduction, dioxindol loses an atom of oxygen, yielding *oxindol*, C_8H_7NO: —

$$\underset{\text{Dioxindol.}}{C_8H_7NO_2} + H_2 = \underset{\text{Oxindol.}}{C_8H_7NO} + H_2O.$$

The constitution of indigo is deduced from a consideration of a number of facts. In the first place, its vapor density shows that it has the molecular weight represented by the formula $C_{16}H_{10}N_2O_2$.

Its relations to isatine, $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO$, make it probable that indigo contains two groups, $C_6H_4<\begin{matrix}C\\N\end{matrix}>C=$, united. It can be made, for example, by reducing isatine chloride, $C_6H_4<\begin{matrix}CO\\N\end{matrix}\!\!>CCl$, a reaction that can be most readily interpreted thus: —

$$C_6H_4<\begin{matrix}CO\\N\end{matrix}\!\!>CCl + 4\ H = C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C : C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4 + 2\ HCl.$$

Further, indigo can be made from di-*o*-nitro-di-acetylene, $C_6H_4 < \begin{matrix} C \equiv C - C \equiv C \\ NO_2 \qquad NO_2 \end{matrix} > C_6H_4$, a fact that shows that the union between the two halves of the indigo molecule is between carbon atoms. The presence of two imino groups is shown by introducing radicals, and then decomposing the ethers thus formed. It is found that the radicals are given off in combination with nitrogen in the form of substituted ammonias.

All these facts, and all others that have been established by the investigations on indigo, are in harmony with the view expressed by the formula for indigo already given: —

$$C_6H_4 < \begin{matrix} CO \\ NH \end{matrix} > C : C < \begin{matrix} CO \\ NH \end{matrix} > C_6H_4.$$

CHAPTER XIX.

HYDROCARBONS CONTAINING TWO BENZENE RESIDUES IN DIRECT COMBINATION.

Just as the marsh-gas residue, methyl, CH_3, unites with methyl to form ethane, $\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}$, so the benzene residue, phenyl, C_6H_5, unites with phenyl to form the hydrocarbon, diphenyl, $\begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix}$, and residues of toluene and of the higher members of the series unite in a similar way to form homologues of diphenyl.

Diphenyl, $C_{12}H_{10}(C_6H_5.C_6H_5)$. — This hydrocarbon is made by treating brom-benzene with sodium: —

$$2\,C_6H_5Br + 2\,Na = C_{12}H_{10} + 2\,NaBr;$$

and by conducting benzene through a tube heated to redness: —

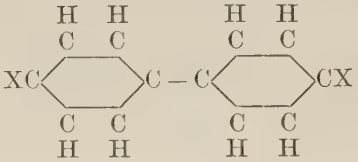
$$2\,C_6H_6 = C_{12}H_{10} + H_2.$$

It forms large, lustrous plates. It melts at 70.5°, and boils at 254°. It is easily soluble in hot alcohol and ether.

Diphenyl is an extremely stable substance. It resists the action of ordinary oxidizing agents, but with strong ones it yields benzoic acid. A large number of derivatives of diphenyl have been studied.

Substitution products of diphenyl. — Substituting agents as the halogens, nitric and sulphuric acids, act upon diphenyl much in the same way as they do upon toluene. Of the mono-substitution products, three varieties, ortho, meta, and para, are possible. Of these the para derivatives are most easily

obtained by the direct action. At the same time ortho derivatives are formed to some extent. By further action ortho-para products and di-para products are formed. In the latter the substituting atoms or groups occupy the positions indicated below: —



Benzidine, $\begin{matrix} C_6H_4 . NH_{2(p)} \\ | \\ C_6H_4 . NH_{2(p)} \end{matrix}$. — This is dipara-diamino-diphenyl. It is formed by reduction of dinitro-diphenyl, and also by the reduction of azobenzene in acid solution. In the latter case hydrazobenzene, which is isomeric with benzidine, is first formed, and this is then transformed into benzidine in the presence of acids (see hydrazobenzene): —

$$\begin{matrix} C_6H_5 . NH \\ | \\ C_6H_5 . NH \end{matrix} \longrightarrow \begin{matrix} C_6H_4 . NH_2 \\ | \\ C_6H_4 . NH_2 \end{matrix}$$

Hydrazobenzene. Benzidine.

Benzidine is manufactured on the large scale by this method. It is a solid that melts at 122°.

The amino groups are in the two para positions in benzidine.

Benzidine dyes. — Benzidine, being an amino derivative of an aromatic hydrocarbon, is readily diazotized, and the final product of the action of nitrous acid is a compound containing two diazo groups or a tetrazo compound. Thus the chloride gives a tetrazo chloride: —

$$\begin{matrix} C_6H_4 . NH_2 . HCl \\ | \\ C_6H_4 . NH_2 . HCl \end{matrix} \longrightarrow \begin{matrix} C_6H_4 . N_2Cl \\ | \\ C_6H_4 . N_2Cl \end{matrix}$$

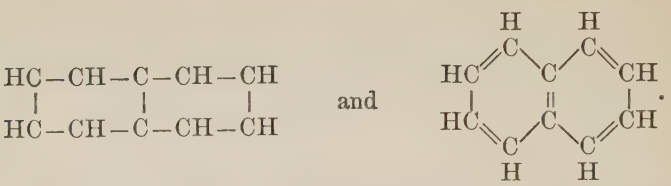
The tetrazo compound reacts with great ease with aromatic amino-sulphonic acids, hydroxy-acids, and phenol-sulphonic acids, forming valuable dyes that have the power to unite directly with cotton. They are called *substantive dyes.* The first dye of this kind that came into use was known as *Congo red.* This is made by treating diphenyltetrazonium chloride with *sodium naphthionate.* Naphthionic acid, as will be shown further on, is a derivative of naphthalene (which see).

Chrysamin is made by the action of sodium salicylate on diphenyltetrazonium chloride: —

$$\begin{matrix} C_6H_4 . N_2Cl \\ | \\ C_6H_4 . N_2Cl \end{matrix} + \begin{matrix} C_6H_4{<}^{OH}_{CO_2Na} \\ C_6H_4{<}^{OH}_{CO_2Na} \end{matrix} = \begin{matrix} C_6H_4 . N_2 . C_6H_3{<}^{OH}_{CO_2Na} \\ | \\ C_6H_4 . N_2 . C_6H_3{<}^{OH}_{CO_2Na} \end{matrix} + 2\,HCl.$$

Carbazol, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$, is a curious derivative of diphenyl that is found in coal tar in small quantity. It has been shown to be a substituted ammonia containing a residue of diphenyl. It is properly designated by the name *diphenyl-imide,* and is represented by the formula $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$. It has been made synthetically by passing the vapor of diphenyl amine, $NH\{^{C_6H_5}_{C_6H_5}$, through a red-hot tube, a reaction taking place which is analogous to that mentioned above as taking place when benzene is treated in the same way, the product in the latter case being diphenyl.

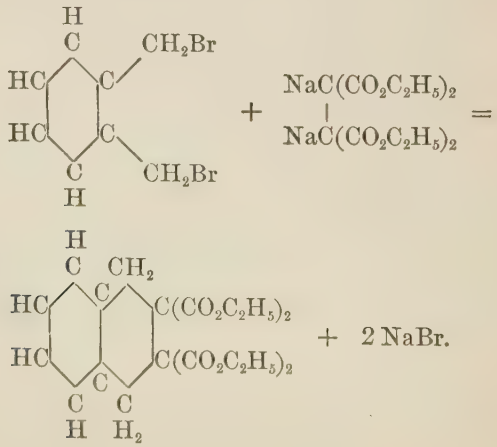
Naphthalene, $C_{10}H_8$. — While the relations of diphenyl to benzene are clearly shown by its simple synthesis from brombenzene, the relations of napthalene to benzene have been discovered through a careful study of its chemical conduct. The facts can be best interpreted by assuming that the molecule of naphthalene is formed by the union of two benzene residues in such a way that they have two carbon atoms in common, as represented in the formulas

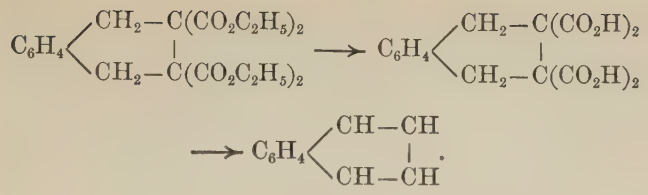


How this conception was reached will be shown below, after the properties and the reactions of naphthalene shall have been discussed.

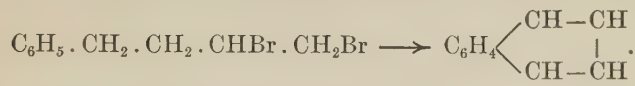
Naphthalene is a frequent product of the heating of organic substances. Thus, it is formed by passing the vapors of alcohol, ether, acetic acid, volatile oils, petroleum, benzene, toluene, etc., through red-hot tubes; and, also, by treating ethylene and acetylene in the same way. It is therefore found in coal tar, and in gas-pipes used for gas made by heating naphtha, gasoline, etc., to high temperatures. It has been made synthetically: —

1. By treating *o*-xylylene bromide with the sodium compound of ethyl acetylene-tetra-carbonate; saponifying the ester thus formed; and distilling the silver salt of the resulting acid: —

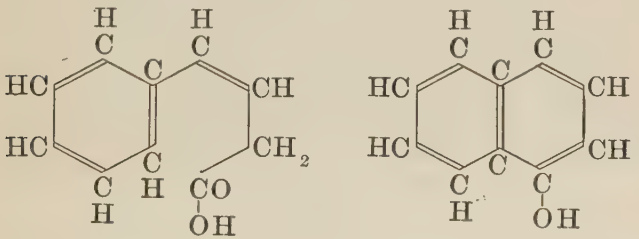




2. By conducting phenyl-butylene bromide over heated lime: —



3. When isophenylcrotonic (phenylvinylacetic) acid, $C_6H_5.CH=CH.CH_2.COOH$, is heated, it loses water and gives α-naphthol, a hydroxyl derivative of naphthalene: —



By reduction with zinc dust α-naphthol gives naphthalene.

The above syntheses give a clew to the constitution of naphthalene, but they do not clear it up entirely. A study of the chemical conduct of naphthalene has, however, led to a solution of the problem.

Napthalene is prepared on the large scale from those portions of coal tar which boil between 180° to 250°. This material is treated with caustic soda, and then with sulphuric acid, and distilled with water vapor.

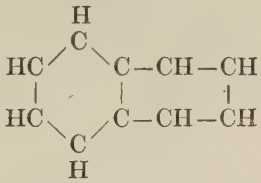
It forms colorless, lustrous, monoclinic plates. It melts at 80°, and boils at 218°. It has a pleasant odor; is volatile with water vapor, and sublimes readily. It is insoluble in water; easily soluble in boiling alcohol, from which it can be crystallized. Oxidizing agents convert it into phthalic acid (see Exp. 74). On the large scale phthalic acid is made from it by oxidizing with sulphuric acid, as has already been stated. It is used as an antiseptic and insecticide. The well-known *moth balls*, for example, are made of naphthalene.

The ease with which naphthalene yields phthalic acid, suggests that the hydrocarbon is probably a di-derivative of benzene containing two hydrocarbon residues; such, for example, as is represented by the formula $C_6H_4\begin{cases}C_2H_2\\C_2H_2\end{cases}$. Such a substance, however, contains unsaturated paraffin residues, and hence ought readily to take up bromine, hydrobromic acid, etc. Bromine and chlorine are indeed taken up easily, but the products thus obtained act rather like the addition-products of benzene than the addition-products of the unsaturated paraffins. They break up readily, and yield stable substitution-products of naphthalene.

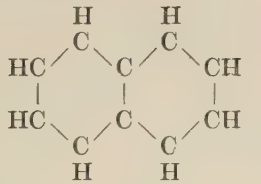
We have seen that a hydrocarbon containing a benzene residue and an unsaturated paraffin residue, as, for example, styrene or phenyl-ethylene, $C_6H_5.C_2H_3$, and phenyl-acetylene, $C_6H_5.C_2H$, when treated with bromine or hydrobromic acid, takes them up as readily as ethylene and acetylene, and this action takes place before substitution. According to this, naphthalene ought to take up bromine and especially hydrobromic acid with avidity before substitution of its hydrogen takes place.

While it does take up four atoms of chlorine or of bromine, it does not take hydrochloric or hydrobromic acid, a fact that makes it improbable that naphthalene contains unsaturated paraffin residues

The formula $C_6H_4\left\{\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right.$ and similar ones being thus rendered extremely improbable, the next thought that suggests itself is that the two groups C_2H_2 may be united, as represented in the formula $C_6H_4\left\{\begin{matrix}CH.CH\\|\\CH.CH\end{matrix}\right.$. Assuming, further, that the two groups are united to two carbon atoms of the benzene residue which are in the ortho relation to each other, we may write this same formula thus: —

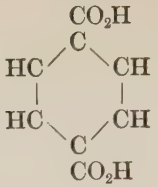


or, what is the same thing, —

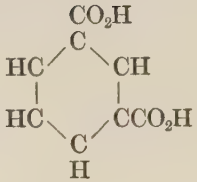


This formula represents naphthalene as made up of two benzene residues united in such a way that they have two carbon atoms in common. This, as has been stated, represents the hypothesis at present held in regard to the nature of naphthalene.

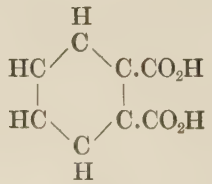
As regards the assumption that the two residues are united through carbon atoms which are in the ortho position relatively to each other, it should be said that this assumption is made because phthalic acid is the product of oxidation; and the facts already considered have shown us that terephthalic acid must be represented by the formula



and isophthalic acid by



and hence, in terms of the accepted hypothesis, the third possible formula must be given to phthalic acid; viz., —



Are there any facts besides those above mentioned which make the hypothesis appear probable?

By a different line of reasoning, based upon other facts, the conclusion is reached that naphthalene is made up of two benzene residues which have two carbon atoms in common, and the only formula which represents this conception is the one already given. The facts which lead to this conclusion are the following: —

When nitro-naphthalene is oxidized it yields nitro-phthalic acid. This shows that the nitro group is contained in a benzene residue; and we may represent it by the formula

$C_6H_3.NO_2\begin{cases}C_2H_2\\C_2H_2\end{cases}$, the oxidation taking place as indicated thus:—

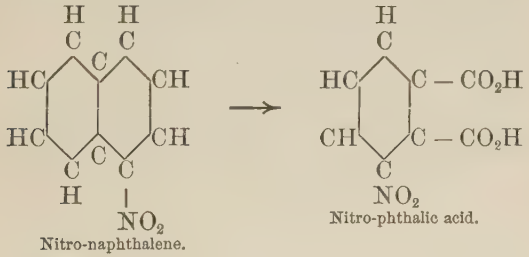
$$C_6H_3.NO_2\begin{cases}C_2H_2\\C_2H_2\end{cases}+9\,O=C_6H_3.NO_2\begin{cases}CO_2H\\CO_2H\end{cases}+H_2O+2\,CO_2.$$

By reducing this same nitro-naphthalene, amino-naphthalene is obtained; and, when this is oxidized, phthalic acid is formed:—

$$C_6H_4\begin{cases}C_2H.NH_2\\C_2H_2\end{cases}+12\,O=C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}+2\,CO_2+HNO_3+H_2O.$$

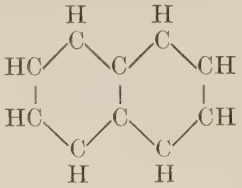
These two reactions show (1) that the part of nitro-naphthalene in which the nitro group is situated is a benzene residue; (2) that there is another benzene residue in the compound into which the nitro group has not entered.

These transformations may be represented thus:—

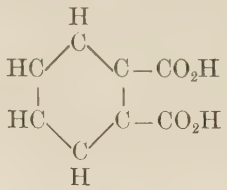


It has been noticed, also, that by oxidation of a naphthalene-sulphonic acid, both sulpho-phthalic and phthalic acid itself are obtained.

It follows, from these facts, that naphthalene is made up of two benzene residues, and the only way in which a hydrocarbon of the formula $C_{10}H_8$ can be thus made up, is by having two carbon atoms common to the two residues, as represented in the formula already given : —



The proof just given for this formula is independent of any notions regarding the ortho, meta, and para relations in benzene. As phthalic acid is the product of oxidation, it follows that the carboxyl groups in the acid must bear to each other the relation expressed by the formula

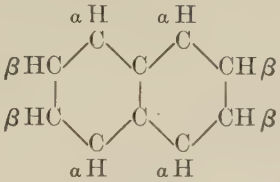


and, therefore, that in all ortho compounds the substituting groups bear this same relation to each other. Hence, by starting with the notion that the above formula represents phthalic acid, — and to this notion, it must be remembered, we are led independently of any facts connected with the formation of the acid from naphthalene, — the accepted formula of naphthalene follows naturally.

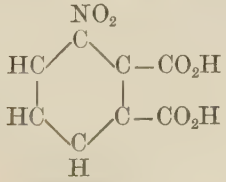
Derivatives of Naphthalene.

An interesting fact that has been discovered by a study of the mono-substitution products of naphthalene is this, — that two, and only two, varieties can be obtained. There is an α- and

a β-chlor-naphthalene, an α- and a β-brom-naphthalene, etc., etc. This fact is quite in harmony with the views held regarding the constitution of naphthalene, as will readily be seen by examining the formula somewhat more in detail We see that there are two, and only two, kinds of relations which the hydrogen atoms bear to the molecule; all those marked with an α being of one kind, and all those marked with a β being of another kind:—

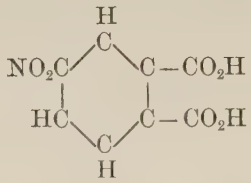


Here, again, a problem presents itself like that of the di-substitution products of benzene. The theory gave us three formulas, and three compounds are known. The problem was, to determine which formula to assign to each compound. Here we have two formulas for two brom-naphthalenes and other mono-substitution products of naphthalene, and we actually have two compounds; and the question arises, which of the two formulas must we assign to a given compound? The method adopted is simple, and can be explained in a few words. That nitro derivative of naphthalene which is known as α-nitro-naphthalene yields nitro-phthalic acid by oxidation; and the relation of the nitro group to the carboxyl groups, in this acid, has been determined. It is expressed by the formula



Formula I.

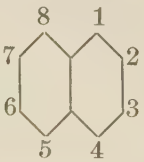
while the formula of the other nitro-phthalic acid is



Formula II.

As α-nitro-naphthalene yields the acid of formula I., it follows that in it the nitro group must occupy the position of one of the hydrogen atoms marked α in the above formula for naphthalene. Those substitution-products of naphthalene which belong to the same series as α-nitro-naphthalene are called α *derivatives.* In the β compounds the substituting group or atom must occupy the place of one of the hydrogen atoms marked β.

According to the theory in every case in which the two substituting atoms or groups are the same, there are ten di-substitution products of naphthalene possible. For example, there are ten di-chlor-naphthalenes possible. *All ten are known and no more.* The relations between the two substituting atoms can be followed by the aid of the figure below: —



The numbers mark the positions of the eight hydrogen atoms in naphthalene. Two substituting atoms or groups may bear to each other the relations

1, 2; 1, 3; 1, 4; 1, 5; 1, 6; 1, 7; 1, 8; 2, 3; 2, 6; 2, 7.

Further there are fourteen tri-substitution-products possible in which the three substituting atoms or groups are the same.

There are fourteen tri-chlor-naphthalenes possible and all are known.

α-Amino-naphthalene, α-naphthylamine, α-$C_{10}H_7 . NH_2$. — This is formed by the reduction of α-nitro-naphthalene, which is the chief product of the treatment of naphthalene with nitric acid in the cold. It melts at 50°. It is also formed from the corresponding hydroxyl compound, α-naphthol, by heating it with the ammonia compound of zinc chloride. It turns red in contact with the air. It has a pungent odor.

β-Amino-naphthalene, β-naphthylamine, β-$C_{10}H_7 . NH_2$, is made from β-naphthol by treating it with the ammonia compound of zinc chloride. It melts at 112° and has no odor.

Several of the sulphonic acids derived from the naphthylamines are of value for the preparation of dyes.

Naphthionic acid, 1, 4, naphthylamine-sulphonic acid. — It is the sodium salt of this acid that gives Congo red when brought together with diphenyltetrazonium chloride (see benzidine): —

$$\begin{array}{l} C_6H_4 . N_2Cl + C_{10}H_6 < \begin{matrix} SO_3Na \\ NH_2 \end{matrix} \\ | \\ C_6H_4 . N_2Cl + C_{10}H_6 < \begin{matrix} SO_3Na \\ NH_2 \end{matrix} \end{array} =$$

$$\begin{array}{l} C_6H_4 . N_2 . C_{10}H_5 < \begin{matrix} SO_3Na \\ NH_2 \end{matrix} \\ | \\ C_6H_4 . N_2 . C_{10}H_5 < \begin{matrix} SO_3Na \\ NH_2 \end{matrix} \end{array} + 2\,HCl.$$

Congo red.

When β-naphthylamine is treated with sulphuric acid, four mono-sulphonic acids are formed.

Naphthols, $C_{10}H_7 . OH$. — Both of the naphthols occur in coal tar. They act in general like the phenols, though the hydroxyl group reacts more readily than that in the phenols. It has already been seen that the amino group can be substi-

tuted for the hydroxyl group of the naphthols. The naphthols are made by fusing the corresponding sulphonic acids with caustic potash: —

$$C_{10}H_7 . SO_3K + KOH = C_{10}H_7 . OH + K_2SO_3.$$

Both sulphonic acids are formed when naphthalene is treated with sulphuric acid. At low temperatures (80°) the α-acid is the chief product. At higher temperatures (160°) the β-acid is formed in larger quantity. Indeed, the α-variety is converted into the β-variety when heated with sulphuric acid.

The synthesis of α-naphthol by heating phenylisocrotonic acid has already been referred to (see page 379).

α-Naphthol is difficultly soluble in water, crystallizes in lustrous needles, and melts at 95°.

β-Naphthol is easily soluble in water, crystallizes in leaflets, and melts at 122°.

Naphthol-sulphonic acids. — Many of these are known, and are used in the preparation of azo dyes. The 1, 4, naphthol-sulphonic acid is the one principally used.

Among the azo dyes derived from naphthalene the following may be mentioned: —

α-Naphthol orange, formed by the action of α-naphthol on the sodium salt of benzene-diazonium sulphonate. It is represented by the formula $C_{10}H_6 < \begin{matrix} N_2C_6H_4SO_3Na(4) \\ OH(1) \end{matrix}$;

β-Naphthol orange, made with β-naphthol in the same way;

Biebrich scarlet, made from β-naphthol by treating it with a diazo compound formed by first diazotizing sulphanilic acid, treating the diazo compound thus obtained with sulphanilic acid, diazotizing the product and treating with β-naphthol. This dye may serve as an example of the possibilities presented by the azo compounds. Its formula is

$$C_{10}H_6 < \begin{matrix} N_2 . C_6H_3 < \begin{matrix} SO_3Na & (1) \\ N_2 . C_6H_4 . SO_3Na & (2) \end{matrix} \\ OH \end{matrix}$$

Poirrier's Orange II. is formed by treating benzene-diazonium sulphonate (see sulphanilic acid) with β-naphthol. Its formula is $C_{10}H_6 < \begin{matrix} N_2 . C_6H_4 . SO_3Na \\ OH \end{matrix}$.

The *Ponceaux* and *Bordeaux dyes* are formed by treating 1, 4, naphthol-sulphonic acid with diazo salts.

Some of the simpler derivatives of naphthalene are used as dyes. Among these the following may be mentioned: —

Di-nitro-naphthol, $C_{10}H_5(NO_2)_2OH$, which is used in the form of the sodium salt under the name of *Martius' Yellow;*

Di-nitro-naphtholsulphonic acid, $C_{10}H_4 \begin{cases} (NO_2)_2 \\ SO_3H \\ OH \end{cases}$, which in the form of the sodium salt is used under the name *Naphthol Yellow S.*

α-Naphtho-quinone, $C_{10}H_6O_2$. — This compound is obtained by oxidizing naphthalene with chromic acid; also by oxidizing α-amino-α-naphthol and other di-substitution products of naphthalene in which the two substituting groups are in the 1, 4 position relatively to each other. It bears to naphthalene the same relation that ordinary quinone bears to benzene; that is, it is naphthalene in which two hydrogen atoms are replaced by two oxygen atoms.

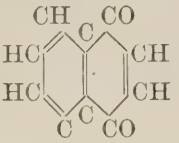
It forms yellow needles, which melt at 125°. Like ordinary quinone, it is volatile with water vapor. Hydriodic acid converts it into *α-hydro-naphtho-quinone:* —

$$C_{10}H_6O_2 + H_2 = C_{10}H_6(OH)_2.$$

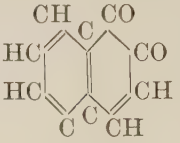
Note for Student. — Compare with the action of reducing agents on ordinary quinone.

β-Naphtho-quinone, $C_{10}H_6O_2$. — This quinone is formed by oxidizing β-amino-α-naphthol with ferric chloride. It consists of red needles that decompose at 115–120°. It is inodorous and is not volatile. While in α-naphtho-quinone the two oxygen atoms are in the 1, 4 (para) position to each other, as they are

in ordinary benzoquinone (see Quinone), in β-naphtho-quinone the oxygen atoms are ortho to each other. α-Naphtho-quinone in general resembles ordinary quinone; β-naphtho-quinone does not. The formulas of the two naphtho-quinones are here given: —



α-Naphtho-quinone.



β-Naphtho-quinone.

Di-hydroxy-naphtho-quinone, $C_{10}H_4\left\{\begin{matrix}(OH)_2\\O_2\end{matrix}\right.$, is a dye known by the name *naphthazarin*, on account of its resemblance to *alizarin* (which see).

Homologues of naphthalene — like methyl- and ethyl-naphthalene — have been prepared. α- and β-Methyl-naphthalene have been found in coal tar.

Quinoline and Analogous Compounds.

When quinine or cinchonine is distilled with caustic potash, a basic substance of the formula C_9H_7N is formed. This is called *quinoline*. It occurs in coal tar together with an isomeric substance *isoquinoline*, and some homologues. Among the compounds homologous with quinoline are the following: —

Quinaldine, α-Methyl-quinoline . . . . $C_{10}H_9N$.
Lepidine, γ-Methyl-quinoline . . . . $C_{10}H_9N$.
Cryptidine . . . . . $C_{11}H_{11}N$.

Quinoline, C_9H_7N. — Quinoline is formed by the distillation of quinine, cinchonine, or strychnine, with caustic potash; is formed from certain derivatives of benzene; and is found in coal tar.

1. By passing allyl-aniline over heated lead oxide: —

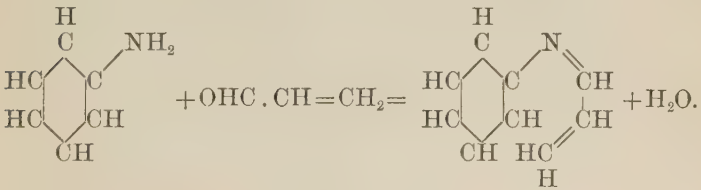
$$C_6H_5 . NH . CH = CH . CH_3 + O_2 = C_9H_7N + 2\,H_2O.$$

This synthesis is similar to that of naphthalene from phenyl-butylene (see p. 379).

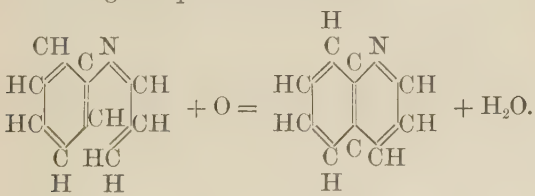
2. By heating together glycerol, aniline, nitro-benzene, and sulphuric acid. In this case acroleïn is probably first formed from the glycerol by the action of the sulphuric acid: —

$$\begin{array}{l} CH_2OH \quad CH_2 \\ | \qquad\quad \| \\ CH\ OH = CH \\ | \qquad\quad | \\ CH_2OH \quad CHO \end{array} + 2\,H_2O.$$

This acroleïn then combines with aniline thus: —



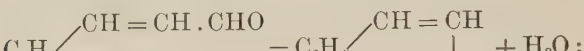
The nitro-benzene now acts as an oxidizer, and removing two hydrogen atoms gives quinoline: —



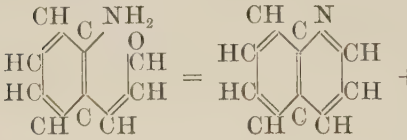
The nitro-benzene in acting as an oxidizing agent is itself reduced, and the aniline thus formed enters into reaction together with the other aniline present. The whole change can be represented as below: —

$$2\,C_6H_5NH_2 + C_6H_5NO_2 + 3\,C_3H_8O_3 = 3\,C_9H_7N + 11\,H_2O.$$

3. From *o*-amino-cinnamic aldehyde by loss of water: —

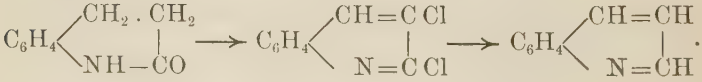


or

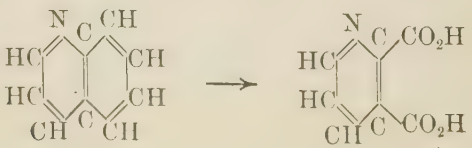


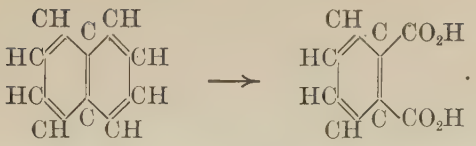
This simple synthesis shows very clearly the constitution of quinoline. It is analogous to naphthalene in a way. Just as the latter is made up of two benzene rings united by two common carbon atoms, so quinoline is made up of a benzene ring and a pyridine ring united in the same way. This hypothesis is in harmony with all the facts known in regard to quinoline.

4. Another synthesis of quinoline is effected by starting with hydrocarbostyril (which see). When this is treated with phosphorus pentachloride it is converted into dichlor-quinoline, and by reduction with hydriodic acid this gives quinoline: —



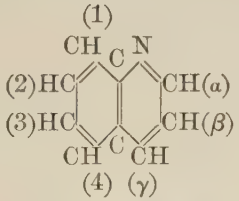
Quinoline is a colorless liquid with a penetrating odor, and is a powerful antiseptic. It boils at 239°. Potassium permanganate converts it into quinolinic acid, which is a pyridine-dicarbonic acid, $C_5H_3N(CO_2H)_2$. The formation of this acid is analogous to the formation of phthalic acid from naphthalene: —





It has already been pointed out that quinolinic acid gives pyridine when distilled with lime and that the accepted hypothesis in regard to the constitution of pyridine is based on this fact and the formation of quinolinic acid from quinoline (see pyridine).

Quinoline forms well-characterized salts with acids. In these salts it acts like a mon-acid base. The number of substitution products derivable from quinoline is large. Thus there are seven mono-substitution-products possible, as will be seen by an examination of the figure below: —



A substituting atom or group may take the place of any one of the hydrogen atoms indicated by the letters α, β, and γ, and the numbers 1, 2, 3, 4, each of which bears a different relation to the nitrogen atom. According to this there are seven possible mono-methyl derivatives. *All of these are known.* So also there are seven possible mono-chlor derivatives, and all of these are known.

The methyl derivatives are designated by the letters α, β, γ, and the numbers 1, 2, 3, 4.

α-**Methyl-quinoline, Quinaldine,** $C_9H_6(CH_3)N$. — This occurs in coal tar, and can be made by digesting aniline, paraldehyde, and hydrochloric acid: —

$$C_6H_5.NH_2 + 2\,C_2H_4O = C_6H_4\begin{cases} CH=CH \\ | \\ N=C(CH_3) \end{cases} + 2\,H_2O + H_2;$$

and by treating *o*-amino-benzoic aldehyde with acetone: —

$$C_6H_4\begin{cases} CHO \\ NH_2 \end{cases} + \begin{matrix} CH_3 \\ | \\ CO-CH_3 \end{matrix} = C_6H_4\begin{cases} CH=CH \\ | \\ N=C-CH_3 \end{cases} + 2\,H_2O.$$

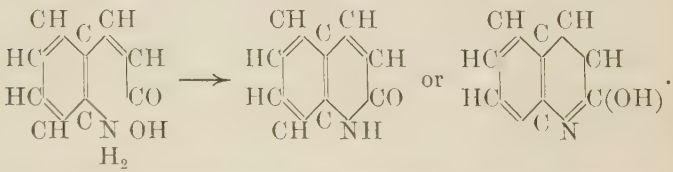
γ-Methyl-quinoline, Lepidine, $C_9H_6(CH_3)N$. — This occurs together with quinoline and quinaldine in coal tar, and it is formed by distilling cinchonine with caustic potash. When this is brought together with iso-amyl iodide an addition-product is formed, and when the latter is treated with caustic potash the substance known as *cyanin* is formed: —

$$2\,C_{10}H_9N.C_5H_{11}N = C_{30}H_{39}N_2I + HI.$$

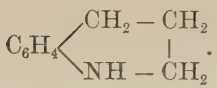
Cyanin forms monoclinic prisms with a metallic green lustre. Its solution in alcohol is deep blue. This color is destroyed by acids and restored by alkalies.

1-Hydroxy-quinoline, $C_6H_3(OH)\begin{cases} N=CH \\ | \\ CH-CH \end{cases}$, is formed from 1-quinoline-sulphonic acid by fusing it with caustic potash.

α-Hydroxy-quinoline, Carbostyril, is formed by the elimination of water from *o*-amino-cinnamic acid. It has either the hydroxyl or the keto group in the pyridine ring: —



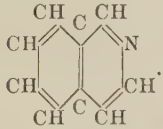
Hydrogen addition-products of quinoline and its derivatives. — Quinoline, like naphthalene, takes up hydrogen quite easily. Tin and hydrochloric acid convert it into tetra-hydro-quinoline, in which the hydrogen has been added to the pyridine ring: —

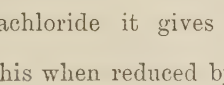


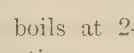
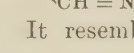
The hydrochloride of 1, hydroxy-methyl-tetra-hydro-quinoline, is used as a febrifuge under the name *kairine*.

The sulphate of 4, methoxy-tetra-hydro-quinoline, called *thalline*, is also used as a febrifuge.

The final product of the addition of hydrogen to quinoline is deca-hydro-quinoline, $C_9H_{18}N$.

Isoquinoline,  . — A base isomeric with quinoline is found with it in coal tar. This base, which is called isoquinoline, can be made by methods that show that the isomerism with quinoline is due to a difference in the position of the nitrogen atom. In it the nitrogen atom is not directly connected with the benzene ring, but it is in the β-position as shown in the above formula. It can be made, for example, from the imide of an acid of the formula $C_6H_4 < \begin{matrix} CH_2.COOH \\ COOH \end{matrix}$ (homophthalic acid). This imide has the formula



By phosphorus pentachloride it gives dichlor-isoquinoline,  , and this when reduced by means of zinc dust gives isoquinoline,  . Isoquinoline melts at 23° and boils at 240.5°. It resembles quinoline in its general properties.

Several alkaloids are derivatives of tetra-hydro-isoquinoline, such, for example, as *papaverine*, *narcotine*, and *hydrastine*.

CHAPTER XX.

HYDROCARBONS CONTAINING TWO BENZENE RESIDUES INDIRECTLY COMBINED.

Diphenyl and naphthalene have been shown to consist of two benzene residues in direct combination. Diphenyl-methane is an example of a hydrocarbon consisting of two benzene residues in indirect combination, $C_6H_5 . CH_2 . C_6H_5$. As diphenyl-methane is closely related to toluene, it was treated of in connection with the hydrocarbons of the benzene series. There are some hydrocarbons which have been shown to consist of two benzene residues united by means of residues of unsaturated paraffins. The most important of these is the well-known anthracene.

Anthracene, $C_{14}H_{10}$. — Anthracene is formed under conditions similar to those which give rise to the formation of naphthalene, especially by heating organic substances to a high temperature, and is hence found in coal tar.

It has been made synthetically from benzene derivatives by a number of methods: —

1. By heating ortho-brom-benzyl bromide with sodium: —

$$2\,C_6H_4\begin{cases}CH_2Br\\Br_{(o)}\end{cases} + 4\,Na = C_{14}H_{10} + 4\,NaBr + 2\,H;$$

or,

$$C_6H_4\begin{cases}CH_2Br\\Br\end{cases} + \begin{matrix}Br\\BrH_2C\end{matrix}\Big\}\,C_6H_4 + 4\,Na$$

$$= C_6H_4\begin{cases}CH\\CH\end{cases}\Big\}\,C_6H_4 + 4\,NaBr + 2\,H.$$

2. By treating a mixture of benzene and acetylene tetrabromide with aluminium chloride: —

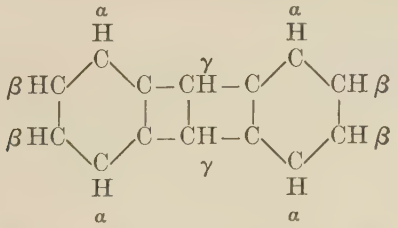
$$C_6H_6 + \begin{matrix} BrCHBr \\ | \\ BrCHBr \end{matrix} + C_6H_6 = C_6H_4 \begin{matrix} CH \\ / \quad \backslash \\ | \quad | \\ \backslash \quad / \\ CH \end{matrix} C_6H_4 + 4\,HBr.$$

Anthracene is prepared in large quantity from those portions of coal tar which boil between 340° and 360°. The distillate is redistilled, and that which remains in the retort after the temperature has reached 350° is treated with liquid sulphur dioxide. When pure it forms laminæ, or monoclinic plates, which are fluorescent. It melts at 213°, and boils at 351°.

Anthracene takes up hydrogen, forming *di-hydro-anthracene*, $C_{14}H_{12}$, and *hexa-hydro-anthracene*, $C_{14}H_{16}$. It takes up bromine and chlorine, forming first addition-products, and then substitution-products.

Oxidizing agents convert anthracene into *anthra-quinone*, $C_{14}H_8O_2$, just as they convert naphthalene into naphthaquinone.

The formation of anthracene from ortho-brom-benzyl-bromide and from benzene and acetylene tetrabromide (see above) furnishes strong proof in favor of the view that anthracene consists of two groups, C_6H_4, united by the group, C_2H_2; thus, $C_6H_4.C_2H_2.C_6H_4$. It hence appears as a diphenylene[1] derivative of ethane, $C_2H_2(C_6H_4)_2$, analogous to diphenyl-ethane, $C_2H_4(C_6H_5)_2$. This conception may also be expressed thus: —



This is the formula commonly accepted for anthracene. It is in harmony with a large number of facts, and has been an efficient aid in investigations on anthracene and its derivatives.

[1] Phenylene = C_6H_4.

The Greek letters α, β, γ, show the three different positions of the hydrogen atoms, and indicate that there are three possible mono-substitution-products of anthracene.

Anthraquinone, $C_{14}H_8O_2\left(=C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4\right)$. — Anthraquinone is formed

1. By direct oxidation of anthracene: —

$$C_{14}H_{10} + O_3 = C_{14}H_8O_2 + H_2O.$$

2. By distilling calcium benzoate: —

$$C_6H_4<\begin{matrix}COOH\ H\\H\ HOOC\end{matrix}>C_6H_4 = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + 2\,H_2O.$$

3. By treating phthalyl chloride, $C_6H_4<\begin{matrix}COCl\\COCl\end{matrix}$[1], with benzene in the presence of aluminium chloride: —

$$C_6H_4<\begin{matrix}COCl\\COCl\end{matrix} + C_6H_6 = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + 2\,HCl.$$

4. By distilling calcium phthalate: —

$$\left.\begin{matrix}C_6H_4\{\begin{matrix}COO\\CO\end{matrix}>Ca\\C_6H_4\{\begin{matrix}CO\\COO\end{matrix}>Ca\end{matrix}\right\} = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + 2\,CaCO_3$$

[1] It has already been pointed out that diphenyl-phthalid is also formed from phthalyl chloride, benzene, and aluminium chloride. Diphenyl-phthalid is related to anthraquinone, as shown by the formulas

$$C_6H_4<\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}>O \quad \text{or} \quad C\{\begin{matrix}C_6H_5\\C_6H_5\\C_6H_4.CO\\O\text{——}\end{matrix}$$

Diphenyl-phthalid.

and

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$$

Anthraquinone.

The formation of these two substances from phthalyl chloride shows either that phthalyl chloride itself is a mixture of two isomeric chlorides, $C_6H_4<\begin{matrix}COCl\\COCl\end{matrix}$ and $C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$, or that it can act in both ways, showing thus the phenomenon of tautomerism.

Experiment 80. Dissolve 5g commercial anthracene in 220cc hot glacial acetic acid. Slowly add to the boiling solution 50g chromic acid in 50cc acetic acid (50 p. c.). Boil for some hours. After cooling, add 750cc water; filter; wash; dry; and sublime.

Anthraquinone forms rhombic crystals, melting at 285°. It sublimes in yellow needles; is insoluble in water, but slightly soluble in alcohol and ether. It is an extremely stable compound, resisting the action of alcoholic potash and oxidizing agents. Melted with solid potassium hydroxide, it yields benzoic acid: —

$$C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > C_6H_4 + 2\,KOH = 2\,C_6H_5 . COOK.$$

Reducing agents convert it successively into *oxanthranol*, $C_{14}H_{10}O_2$, *anthranol*, $C_{14}H_{10}O$, and *anthracene*, $C_{14}H_{10}$. These changes may be represented thus: —

$$C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > C_6H_4 + H_2 \qquad = C_6H_4 < \underset{\text{Oxanthranol.}}{\begin{matrix} CH(OH) \\ CO \end{matrix}} > C_6H_4;$$

$$C_6H_4 < \begin{matrix} CH(OH) \\ CO \end{matrix} > C_6H_4 + H_2 = C_6H_4 < \underset{\text{Anthranol.}}{\begin{matrix} C(OH) \\ \vert \\ CH \end{matrix}} > C_6H_4 + H_2O;$$

$$C_6H_4 < \begin{matrix} C(OH) \\ CH \end{matrix} > C_6H_4 + H_2 \qquad = C_6H_4 < \begin{matrix} CH \\ \vert \\ CH \end{matrix} > C_6H_4 + H_2O.$$

When heated with zinc dust, it yields anthracene. A great many derivatives of anthraquinone have been made. Among the best known are the hydroxyl derivatives, some of which are much-prized dyes and are manufactured in great quantities.

The hydroxyl derivatives of anthraquinone can be made by melting either the bromine derivatives or the sulphonic acids with caustic potash.

Alizarin, Di-hydroxy-anthraquinone, } $C_{14}H_8O_4[=C_{14}H_6O_2(OH)_2]$.

Alizarin is the well-known dye that was originally obtained from madder root. The substance found in the root is *ruberythric acid*, a glucoside of the formula $C_{26}H_{28}O_{14}$. When this is treated with dilute acids or alkalies or ferments, it is decomposed, yielding alizarin and a glucose: —

$$C_{26}H_{28}O_{14} + 2\,H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2\,\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

It is formed by melting dichlor- or dibrom-anthraquinone or anthraquinone-monosulphonic acid with caustic potash: —

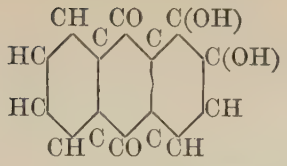
$$C_{14}H_7O_2.SO_3K + KOH + O = C_{14}H_6O_2(OH)_2 + K_2SO_3.$$

Alizarin is now manufactured from anthracene on the large scale, and large tracts of land that were formerly used for cultivating madder are now used for other purposes.

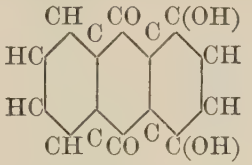
Experiment 81. Dissolve 20g anthraquinone in a small quantity of fuming sulphuric acid, heating gradually to 260°. Dissolve the product in a litre of water. Neutralize with finely-powdered chalk; filter. Precipitate with a solution of sodium carbonate; filter; and finally evaporate to dryness. The salt thus obtained is impure sodium anthraquinone-monosulphonate. In an iron crucible mix 10g of the sulphonate, 40g sodium hydroxide, and 3g potassium chlorate, and heat for several hours at 165° to 175°. The formation of alizarin, during the melting, is shown by the dark-purple color of the mass. When a little of this is dissolved in water, it should form a beautiful purple-red solution. Continue the melting until the mass acts in this way. Dissolve the mass in $\frac{3}{4}$l to 1l water, and acidify. Alizarin is thrown down in brown amorphous flakes. Filter off, dry, and sublime between watch-glasses.

Alizarin forms red needles, which melt at 289°. It dissolves in alkalies, forming dark purple-red solutions. When heated with zinc dust, it yields anthracene. It was this reaction which gave the first clew to the nature of alizarin, and led, soon after, to its synthesis.

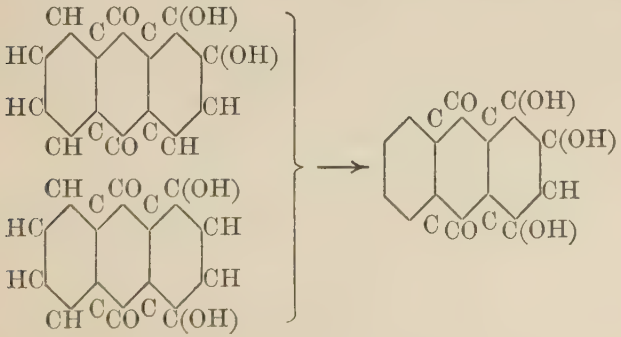
The two hydroxyl groups in alizarin are in the α and β positions in one benzene ring, as shown in the formula



The evidence in favor of this view is this: Alizarin is formed by heating pyrocatechol and phthalic anhydride with sulphuric acid. This shows that the two hydroxyl groups are in the ortho position with reference to each other. It is only necessary to show that one of the hydroxyls is in the α position to make the evidence complete. A second di-hydroxy-anthraquinone known as *quinizarin* is formed from phthalic anhydride and hydroquinol. In quinizarin, therefore, the hydroxyl groups are in the para position with reference to each other, —



When quinizarin is oxidized, a third hydroxyl group is introduced, and purpurin, a trihydroxy-anthraquinone, is formed. The same is true of alizarin. It follows therefore that in alizarin the hydroxyl groups are in the α and β positions: —



There are ten possible di-hydroxy-anthraquinones. Nine of these are known. Those in which the hydroxyl groups are in the ortho relation to each other have coloring power.

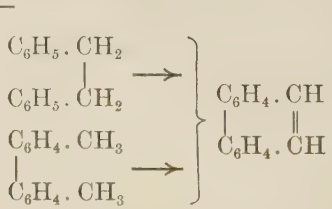
Purpurin, Tri-hydroxy-anthraquinone, $C_{14}H_5O_5=[C_{14}H_5O_2(OH)_3]$.

Purpurin is contained in madder root, and is therefore found in madder alizarin. It can be made by melting alizarin-sulphonic acid with caustic potash, by melting tri-bromanthraquinone with caustic potash, and also by oxidizing alizarin or quinizarin with manganese dioxide and sulphuric acid.

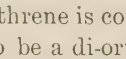
It dissolves in water, forming solutions that are pure red. With alumina mordants it gives a beautiful scarlet red.

Anthrapurpurin, isopurpurin, $C_{14}H_5O_2(OH)_3$, is found in artificial alizarin.

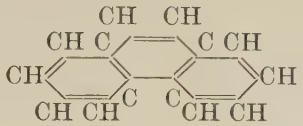
Phenanthrene, $C_{14}H_{10}$, which is isomeric with anthracene, is also found in the higher boiling parts of coal tar. It is found further in "stupp," a mixture of substances obtained in the distillation of mercury ores in Idria. It is formed from dibenzyl and from *o*-ditolyl by passing their vapors through red-hot tubes: —



When oxidized, phenanthrene is converted into diphenic acid, which has been shown to be a di-ortho carboxyl derivative of diphenyl, —



In this process phenanthraquinone is formed as an intermediate product. This bears to phenanthrene the same relation that anthraquinone bears to anthracene. The facts mentioned and all other facts known in regard to phenanthrene make it clear that this hydrocarbon is made up as shown in the formula



It is a derivative of diphenyl, and is made up of three benzene rings. The formation of phenanthraquinone and of diphenic acid by oxidation of phenanthene is easily explained on this assumption.

CHAPTER XXI.

GLUCOSIDES, ALKALOIDS, ETC.—CONCLUSION.

Under the head of the sugars, reference was made (see p. 185) to a class of bodies called *glucosides*, that occur in plants. These substances break down under the influence of dilute acids or enzymes into some variety of sugar and other compounds. Thus, salicin breaks down, according to the equation

$$C_6H_4(OH)CH_2(OC_6H_{11}O_5) + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Salicylic alcohol.}}{C_6H_4(OH)CH_2OH}$$

into glucose and salicylic alcohol, the alcohol corresponding to salicylic acid. Some of the more important glucosides are mentioned below.

Æsculin, $C_{15}H_{16}O_9 + 1\frac{1}{2}\,H_2O$, occurs in the bark of the horse-chestnut tree (*Æsculus hippocastanum*). It breaks down into glucose and æsculetin: —

$$\underset{\text{Æsculin.}}{C_{15}H_{16}O_9} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Æsculetin.}}{C_9H_6O_4}.$$

Its water solution shows blue fluorescence.

Amygdalin, $C_{20}H_{27}NO_{11} + 3\,H_2O$, occurs particularly in bitter almonds; also, in the kernels of apples, pears, peaches, plums, cherries, etc. With emulsin, which is an aqueous extract of almonds, amygdalin is broken down into benzoic aldehyde, hydrocyanic acid, and glucose: —

$$C_{20}H_{27}NO_{11} + 2\,H_2O = C_7H_6O + CNH + 2\,C_6H_{12}O_6.$$

Helicin, $C_{13}H_{16}O_7 + \frac{3}{4}\,H_2O$, is formed by the oxidation of salicin (which see). It has also been made artificially by

mixing an alcoholic solution of acetochlorhydrose with the potassium compound of salicylic aldehyde: —

$$C_6H_7ClO_5(C_2H_3O)_4 + C_7H_5O_2K + 4\,C_2H_6O$$
$$= C_{13}H_{16}O_7 + KCl + 4\,C_2H_5 . C_2H_3O_2.$$

Acetochlorhydrose is formed by heating glucose with an excess of acetyl chloride.

Helicin breaks up into glucose and salicylic aldehyde.

Myronic acid, $C_{10}H_{19}NS_2O_{10}$, is found in the form of the potassium salt in black mustard seed. When treated with myrosin, which is contained in the aqueous extract of white mustard seed, potassium myronate is converted into glucose, allyl mustard oil, and acid potassium sulphate: —

$$C_{10}H_{18}NS_2O_{10}K = C_6H_{12}O_6 + C_3H_5 . NCS + KHSO_4.$$

Salicin, $C_{13}H_{18}O_7$, occurs in willow bark, and in the bark and leaves of poplars. Its decomposition into salicylic alcohol and glucose has been referred to (see preceding page).

Saponin, $C_{32}H_{54}O_{18}$, is found in soap root (*Saponaria officinalis*). Its water solution forms a lather like that formed by soap.

Alkaloids.

The alkaloids are compounds occurring in plants, frequently constituting those parts of the plants which are most active when taken into the animal body. They are hence sometimes called the *active principles* of the plants. Many of these substances are used in medicine. As regards their chemical character, they are basic in the sense that ammonia is basic; they contain nitrogen, and form salts, just as ammonia does, *i.e.*, by direct addition to the acids. These and other facts lead to the belief that the alkaloids are related to ammonia — that they are substituted ammonias. Recently it has been shown that several of the alkaloids are related to pyridine (see p. 342) and

quinoline (see p. 390). Only a few of the more important alkaloids need be mentioned here.

Alkaloids of Peruvian Bark.

Quinine, $C_{20}H_{24}N_2O_2 + 3\,H_2O$. — This valuable substance is obtained from the outer bark of the *Cinchona* varieties. When oxidized, it yields derivatives of pyridine. In view of the interest connected with quinine, the discovery of its relation to pyridine and quinoline has led to a large number of investigations on the derivatives of these two bases, and it is probable that before long it will be possible to make quinine synthetically in the laboratory.

The salts of quinine are formed by direct addition of the base to the acids. Thus, we have

Quinine hydrochloride . $C_{20}H_{24}N_2O_2 . HCl$;
Quinine nitrate . . . . . $C_{20}H_{24}N_2O_2 . HNO_3$;
Quinine sulphate . . . $C_{20}H_{24}N_2O_2 . H_2SO_4$, etc., etc.

Cinchonine, $C_{19}H_{22}N_2O$, cinchonidine, $C_{19}H_{22}N_2O$, and other bases occur with quinine in Peruvian bark.

Cocaine, $C_{17}H_{21}NO_4$, is found in coca leaves (*Erythroxylon coca*). It melts at 98° and is levo-rotatory. Its hydrochloric acid salt, $C_{17}H_{21}NO_4 . HCl$, has recently come into prominence in medicine, owing to the fact that it is a powerful anæsthetic.

Nicotine, $C_{10}H_{14}N_2$, occurs in tobacco leaves in combination with malic acid. Potassium permanganate converts it into nicotinic acid, which is one of the possible pyridine-monocarbonic acids.

Atropine, $C_{17}H_{23}NO_3$, is found in many varieties of Solanum together with *hyoscyamine* with which it is isomeric. It is produced from the latter by heating the latter and by treating it

with caustic soda. Atropine gives *tropine* and *tropic acid* when boiled with hydrochloric acid or baryta water. Tropic acid has been shown to be α-phenyl-hydracrylic acid,

$$CH_2(OH) - \underset{\displaystyle C_6H_5}{\underset{|}{CH}} - CO_2H.$$

Tropine, $C_8H_{15}NO$, the basic constituent of atropine, has been prepared artificially.

Alkaloids of Opium.

Opium is the evaporated sap which flows from incisions in the capsules of the white poppy (*Papaver somniferum*), before they are ripe. The three principal alkaloids contained in opium are morphine, codeïne, and narcotine.

Morphine, $C_{17}H_{19}NO_3 + H_2O$, is a crystallizable solid which is difficultly soluble in water, alcohol, and ether. When decomposed, it yields pyridine, trimethyl-amine, and phenanthrene, together with other products.

Codeïne, $C_{18}H_{21}NO_3$, is a mono-methyl derivative of morphine and can be prepared from it.

Narcotine, $C_{22}H_{23}NO_7$, has been shown to contain three methyl groups, which are split off, as methyl chloride, when the substance is heated with hydrochloric acid. It is a derivative of tetra-hydro-isoquinoline.

Piperine, $C_{17}H_{19}NO_3$, is contained in black pepper. When treated with alcoholic potash, it breaks down into piperidine and piperic acid: —

$$C_{17}H_{19}NO_3 + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic acid.}}{C_{12}H_{10}O_4}.$$

Piperidine, $C_5H_{11}N$, which, as just stated, is formed by the decomposition of piperine, has been made synthetically by treating pyridine with nascent hydrogen: —

$$\underset{\text{Pyridine.}}{C_5H_5N} + 6\,H = \underset{\text{Piperidine.}}{C_5H_{11}N}.$$

It may therefore be called *hexa-hydropyridine* (see p. 345).

Strychnine, $C_{21}H_{22}N_2O_2$, **and brucine**, $C_{23}H_{26}N_2O_4 + 4\,H_2O$, are two alkaloids that occur in *nux vomica*.

In the animal body occur a large number of complicated substances, the study of which, at this stage, would hardly be profitable. Thus, there are the albumins, caseïns, and fibrin; the coloring-matters of the blood, oxyhæmoglobin, hæmoglobin, etc. A knowledge of these substances is of great importance for physiology, and much progress has been made in this field. The study of albumin in its various forms has been carried on for many years. It has been shown that when the albumins are decomposed, certain amino acids are formed, and a careful study of the products of decomposition under different conditions has given some insight into their chemical character. Much is to be hoped for from continued investigations of these complicated substances.

The study of the composition of animal substances, such as milk, urine, etc., and of the relations of the chemical substances occurring in the body to the processes of life, is the object of *physiological chemistry*. Without a good knowledge of the general chemistry of the compounds of carbon, however, the subjects treated of under the head of Physiological Chemistry cannot be understood.

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